

**REMARKS**

The present invention relates to a vinyl ether group-containing (meth) acrylic ester composition, and methods of producing, handling and purifying same.

In the Office Action dated February 10, 2004, claims 1-21 were rejected under 35 U.S.C. § 103(a) based on Preparation of Tailor-Made Multifunctional Propenyl Ethers by Radical Copolymerization of 2-(1-Propenyl)oxyethyl Methacrylate, *Macromolecules* 1999, 32, 55-59 (Vaneteenkiste) in view of Bauer.

An Interview with the Examiner was conducted on April 13, 2004, for which we thanks the Examiner for his time and consideration. During the Interview, the present claims and the cited references were discussed. Statement of Substance of the Interview is incorporated herein.

In the present Amendment, the specification has been amended to correct a typographical error, in the 3rd full paragraph on page 14, by replacing "other components" with --the vinyl ether group-containing (meth) acrylic ester--. This amendment is further supported by the working Examples, in particular, Examples 27-31. For the Examiner's convenience, Applicants attach herewith a table summarizing the compositions of Examples 1-31.

The specification has also been amended to correct a obvious error, on page 76, line 8, by replacing "the molecular oxygen concentration" with --nitrogen monoxide gas

concentration--. This amendment is further supported by the specification. For example, in the working Example 119, introduction of an 8% (by volume) nitrogen monoxide gas is described on page 75, lines 33-35. In addition, a method of producing a vinyl ether group-containing (meth) acrylic ester in an atmosphere such that a molecular nitrogen monoxide (NO) and/or molecular nitrogen dioxide (NO<sub>2</sub>) concentration in the gaseous phase in the reaction system is 0.01 to 10% by volume on page 34, line 22 to page 36, line 15.

The specification (page 25, line 1) and claim 8 have been amended to correct an obvious error in formula (5), by replacing "R<sup>3</sup>CH-" with -- R<sup>3</sup>CH<sub>2</sub>- --.

Claims 1-3 and 16 have been amended to further recite --wherein said vinyl ether group-containing (meth) acrylic ester composition comprises the radical polymerization inhibitor and the vinyl ether group-containing (meth) acrylic ester as an end product--. This amendment is supported throughout the specification, in particular, in the working Examples.

Claim 3 has been amended to delete the recitation of "both of a radical polymerization inhibitor and a basic compound." Claim 16 has been amended to delete the recitation of "a radical polymerization inhibitor."

Claims 8 and 10 have been amended to recite --R<sup>4</sup> represents a straight, branched or cyclic alkyl groups containing 1 to 8 carbon atoms--. This amendment is supported by the specification, for example, on page 29, lines 13-15.

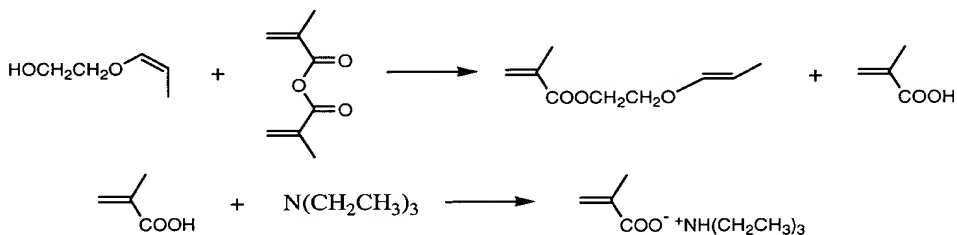
Claims 4 and 9 have been canceled, and claims 22 and 23 have been added. Claims 22 and 23 are supported by the specification, for example, on page 14, 3rd full paragraph as amended and the working Examples, in particular, Example 31.

Claims 1-3, 5-8, 10-14 and 16 have been amended to delete the term "general."

With regard to the §103 rejection, Applicants respectfully traverse, for at least the following reasons.

Claims 1, 2, 3, 16, 18, 19, 20 and 21

Vansteekiste discloses synthesis of 2-(1-propenyl) oxyethyl methacrylate (POMEA). As noted by the Examiner, the reaction mixture contains triethylamine. However, triethylamine is used as a catalyst and neutralizer, and is removed after the reaction. In particular, triethylamine is consumed during the reaction as illustrated below:



Further, the remaining triethylamine if any, is removed after the dichloromethylene solution of the crude product was washed with water, dried, concentrated and distilled in

vacuum to afford the pure product (page 56, left column, last paragraph). For these reasons, the product of Vansteekiste does not contain triethylamine.

As the Examiner pointed out, Bauer discloses that it is often helpful to add a small amount of a polymerization inhibitor. Again, the polymerization inhibitor is added during the reaction for inhibition of polymerization of (meth)acrylic acid lower alkyl ester (col. 5, lines 41-43).

In contrast, present claim 1 as amended specifically recites that the vinyl ether group-containing (meth) acrylic ester in the composition is used as an end product.

Accordingly, even if it might be assumed, *arguendo*, that there might be motivation to use a polymerization inhibitor as disclosed in Bauer in the synthesis process of Vansteekiste, the final product of Vansteekiste would not in any event contain the polymerization inhibitor after workup and purification by vacuum distillation.

In view of the above, the present invention differs from the cited references in that the claimed vinyl ether group-containing (meth) acrylic ester composition of present claim 1 or 2 comprises a radical polymerization inhibitor or a radical polymerization inhibitor and a basic compound, respectively.

With respect to claims 3 and 16, which are directed to a method of producing the vinyl ether group-containing (meth) acrylic ester composition, this method does not include a



step of removing the radical polymerization inhibitor or the basic compound from the composition.

Therefore, the present invention differs from the cited references in that the synthesis of POMEA of Vansteekiste in view of Bauer requires a step of removing triethylamine, which is a basic compound, and/or a radical polymerization inhibitor.

Further, Bauer does not disclose or suggest the specific radical polymerization inhibitors recited in claim 18. During the Interview, the Examiner agreed that the specific radical polymerization inhibitors recited in claim 18 are not disclosed or suggested in the cited references. Accordingly, claim 18 is patentable over the cited references for this reason independently.

Claims 5, 6 and 7

Present claim 5 is directed to a method of handling a vinyl ether group-containing (meth) acrylic ester under the condition such that molecular oxygen concentration in the gaseous phase in contact with a vinyl ether group-containing (meth) acrylic ester is 0.01 to 15% by volume. Present claims 6 and 7 are directed to a method of handling a vinyl ether group-containing (meth) acrylic ester in a lightproof structure.

The Office Action asserted that "One of ordinary skill would recognize that the claimed limitation of water and oxygen content are necessarily met by this reaction."

Applicants respectfully disagree for the following reasons.

In the preparation process of synthesizing 2-(1-propenyl) oxyethyl methacrylate in Vansteenkiste, the reaction product is purified by vacuum distillation. By this procedure, oxygen in the gaseous phase is reduced because of the decrease of air accompanied by pressure decrease and replacement of oxygen with the vapor of the product. Applicants respectfully submit that under these conditions, the oxygen concentration in the gaseous phase in Vansteenkiste falls outside the presently claimed range of 0.01 to 15% by volume.

Thus, some operation, such as introduction of oxygen from outside, or generation of oxygen gas during vacuum distillation, is necessary to keep the oxygen content in a certain region. However, such operation is not disclosed or suggested in Vansteenkiste.

Furthermore, the term “handling” is defined in the 1st full paragraph of page 15 of the specification, which excludes a transient “handling” such as that during vacuum drawing.

During the Interview, the Examiner stated that the term “handling” is construed broadly to read on “concentrating” or “distilling” a composition for a transient moment. Applicants respectfully disagree and urge the Examiner to interpret the meaning of “handling” as defined on page 15 of the specification.

In addition, Vansteenkiste fails to disclose or suggest using a lightproof structure in handling vinyl ether group-containing (meth) acrylic ester. During the Interview, the

Examiner stated that the term "structure" is construed broadly, so that it may include a building where a vinyl ether group-containing (meth)acrylic ester in a container is stored.

Applicants respectfully disagree and urge the Examiner to interpret the meaning of "structure" in light of the specification. The examples of "lightproof structure" is described on 2nd full paragraph of page 18, such as tank lorries for transportation; tanks, drums, bottles and cans for storage; pipes, nozzles and valves for transfer; and reaction vessels, tanks and containers for mixing and stirring. This definition does not encompass a building where a vinyl ether group-containing (meth)acrylic ester in a container is stored.

Further, as described on page 22 of the present specification, last paragraph, the regulation of oxygen content, use of a lightproof structure or the combination of them is a very useful method to produce vinyl ether group-containing (meth) acrylic ester safely and effectively.

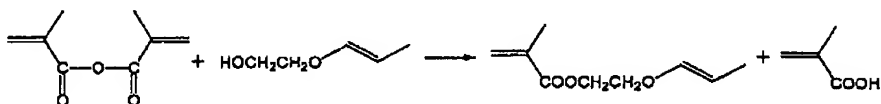
Vansteenkiste is silent on the importance of such aspect.

The present invention is achieved by optimization of a method of handling vinyl ether group-containing (meth) acrylic ester, and shows superior results and unexpected advantages as compared to the prior art.

In view of the above, Applicants respectfully submit that the present claims 5, 6 and 7 are patentable over Vansteenkiste in view of Bauer, because Bauer does not rectify the deficiencies of Vansteenkiste.

Claims 8 and 10

Vansteenkiste discloses a synthesis of POMEA and the reaction is illustrated as follows:



This is a reaction between an acid anhydride and an alcohol.

In contrast, present claims 8 and 10 recite an ester exchange reaction. When POMEA is synthesized by this reaction, the reaction is illustrated as follows:



This is a reaction between an ester and an alcohol.

It is known that the acid anhydride described in Vansteenkiste is a reactive compound and readily reacts with other compounds, whereas the ester of the present invention is not a reactive compound. Applicants attach herein copies of pertinent pages of the following

publications which show the differences in reactivity of an acid anhydride and an ester.

These references clearly show that an acid anhydride is reactive and an ester is not.

(1) Ullmann's Encyclopedia of Industrial Chemistry, Fifth, Completely Revised Edition;

(2) ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, Fourth Edition;

(3) Canadian Patent Publication No. 2,108,627; and

(4) U.S. Patent No. 5,744,613.

(1) describes esterification of an acid anhydride in §5.4. at page 574, and esterification of an ester by an ester exchange reaction in §5.5. at page 575. (2) describes esterification of an acid anhydride on page 768 and esterification of an ester by an ester exchange reaction on page 774. The fact that esterification of an acid anhydride and an ester is described in separate sections indicates that these reactions are different.

(3) discloses a production method from an acid anhydride and a production method from an ester as quite different ones. (4) discloses the production of a product from an acid anhydride, which otherwise can not be produced by an ester exchange reaction. The disclosure in (3) and (4) also indicates that esterification of an acid anhydride and esterification of an ester by an ester exchange reaction are quite different.

In view of the above, the present invention differs from the reaction in Vansteenkiste in that the reaction of Vansteenkiste is a reaction of an acid anhydride, whereas the of present invention involves the reaction of an ester.

Claims 10, 11 and 12

The present claims 10, 11 and 12 are directed to a method of producing a vinyl ether group-containing (meth) acrylic ester in an atmosphere of a certain molecular oxygen concentration, in a lightproof structure, or both. As described above, the regulation of the oxygen content, use of a lightproof structure, or the combination of both is a very useful method to produce vinyl ether group-containing (meth) acrylic ester safely and effectively.

However, the cited references disclose nothing specifically with respect to oxygen content and use of a lightproof structure, nor do they focus on the importance of such aspect, as set forth above.

Claims 13, 14, 15 and 17

Claims 13 and 14 are directed to a method of purifying a vinyl ether group-containing (meth) acrylic ester in an atmosphere such that a molecular oxygen concentration in the gaseous phase in the purification system is 0.01 to 10% by volume, or in a lightproof structure in an atmosphere such that a molecular oxygen concentration in the gaseous phase in the purification system is 0.01 to 15% by volume.

As described above, the regulation of oxygen content, use of a lightproof structure, or the combination of both is a very useful method of producing vinyl ether group-containing (meth) acrylic ester safely and effectively, and is also a very useful method of purifying it.

AMENDMENT UNDER 37 C.F.R. § 1.114  
U.S. Appln. No.: 09/982,861  
Attorney Docket No.: Q66372

In contrast, the cited references disclose nothing specifically with respect to the oxygen content or use of a lightproof structure, nor do they focus on the importance of such aspects as set forth above.

In view of the foregoing, Applicants respectfully submit the present invention is not obvious over the cited references, and the rejection should be withdrawn.

In view of the above, reconsideration and allowance of claims 1-3, 5-8 and 10-21 are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,



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WASHINGTON OFFICE

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Examples of the present invention

	Vinyl ether group-containing (meth) acrylic ester		Radical polymerization inhibitor		Basic compound		Other component		The composition of the present invention
Example 1	VEA	100g	MEHQ	10mg					100wt%
Example 2	VEA	100g	PTZ	10mg					100wt%
Example 3	VEM	100g	HQ	10mg					100wt%
Example 4	VEM	100g	TEMPO	10mg					100wt%
Example 5	VEEA	100g	HEHQ	10mg					100wt%
Example 6	VEEA	100g	TEMPO	10mg					100wt%
Example 7	VEEM	100g	MEHQ	10mg					100wt%
Example 8	VEEM	100g	TEMPO	10mg					100wt%
Example 9	VBA	100g	PTZ	10mg					100wt%
Example 10	VBA	100g	TEMPO	10mg					100wt%
Example 11	VBM	100g	MEHQ	10mg					100wt%
Example 12	VBM	100g	PTZ	10mg					100wt%
Example 13	VEA	100g	MEHQ	5mg	NaOH	5mg			100wt%
Example 14	VEA	100g	MEHQ	5mg	TEHA	5mg			100wt%
Example 15	VEA	100g	MEHQ	5mg	NaOH	5mg			100wt%
Example 16	VEA	100g	MEHQ	5mg	TEHA	5mg			100wt%
Example 17	VEEA	100g	MEHQ	5mg	NaOH	5mg			100wt%
Example 18	VEEA	100g	MEHQ	5mg	TEHA	5mg			100wt%
Example 19	VEEM	100g	MEHQ	5mg	NaOH	5mg			100wt%
Example 20	VEEM	100g	MEHQ	5mg	TEHA	5mg			100wt%
Example 21	VBA	100g	MEHQ	5mg	NaOH	5mg			100wt%
Example 22	VBA	100g	MEHQ	5mg	TEHA	5mg			100wt%
Example 23	VBM	100g	MEHQ	5mg	NaOH	5mg			100wt%
Example 24	VBM	100g	MEHQ	5mg	TEHA	5mg			100wt%
Example 25	VEEA	100g	MEHQ	10mg					100wt%
Example 26	VEEM	100g	MEHQ	10mg	TEHA				100wt%
Example 27	VEA	100g	MEHQ	5mg	NaOH	5mg	toluene	100g	50wt%
Example 28	VEA	100g	MEHQ	5mg	NaOH	5mg	toluene	50g	66.7wt%
Example 29	VEA	100g	MEHQ	5mg	NaOH	5mg	toluene	25g	80wt%
Example 30	VEA	100g	MEHQ	5mg	NaOH	5mg	toluene	10g	90.9wt%
Example 31	VEA	100g	MEHQ	5mg	NaOH	5mg	toluene	5g	95.2wt%



# Ullmann's Encyclopedia of Industrial Chemistry

Volumes A 1–A 28: alphabetically arranged articles  
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## Cross References

Dithionites → Sulfites, Thiosulfates, and Dithionites	Electroless Plating → Electrochemical and Chemical Deposition
DNA → Nucleic Acids and Degradation Products	Electronic Ceramics → Ceramics, Electronic
Dodecanol → Fatty Alcohols	Electrophoretic Coating → Paints and Coatings
Driers → Metallic Soaps	Electrophotography → Imaging Technology
Drug Delivery Systems → Pharmaceutical Dosage Forms	Electrostatic Sealing → Glass
Dry Ice → Carbon Dioxide	Elutriation, treated in the B-Series
Drying, Treated in the B-Series	Embedding → Insulation, Electric; → Epoxy Resins
Drying Agents: Drying, treated in the B-Series	Emulsifiers → Emulsions
Dye Carriers → Textile Auxiliaries	Emulsion Polymerization → Polymerization Technology
Dyes, Reactive → Reactive Dyes	Enamel → Ceramics, Ceramic - Metal Systems
Dysprosium → Rare-Earth Metals	Engineering Plastics → Plastics, General Aspects; → Plastics, Properties and Testing
Earthenware → Whitewares	Environmental Protection, treated in the B-Series
Eggs → Food Technology; → Proteins	Epichlorohydrin → Epoxides
Einsteinium → Transuranium Elements	Epinephrine → Hormones
Elastomeric Fibers → Fibers, Synthetic Organic; → Rubber, Natural; → Rubber, Synthetic	Epoxidation → Epoxides
Elastomers → Rubber	Epoxide Polymers → Polyoxyalkylenes
Elastomers, Thermoplastic → Thermoplastic Elastomers	Erbium → Rare-Earth Elements
Electric Cells → Batteries	Essential Oils → Flavors and Fragrances
Electrochemical Machining → Electrochemistry	Estrogens → Hormones
Electrodecantation: Membrane Technology, treated in the B-Series	Ethane → Hydrocarbons

## Esters, Organic

WILHELM RIEMENSCHNEIDER, retired from Hoechst AG, Frankfurt, Federal Republic of Germany

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### 1. Introduction

Organic esters are compounds with the general formula



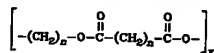
where R<sup>1</sup> and R<sup>2</sup> represent either the same or different aliphatic, aromatic, or heterocyclic groups. Esters are classified as carboxylic acid derivatives; they are prepared mainly by the reaction of a carboxylic acid and an alcohol (esterification).

Ortho esters are derived from ortho acids:



Ortho esters can be hydrolyzed to carboxylic acids and alcohols, but their properties are more similar to those of acetals. They are dealt with briefly in Section 5.12.

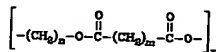
If a molecule possesses both a carboxyl and a hydroxyl group, it may form either polyesters:



or cyclic internal esters (lactones) (Section 5.13):



Ring opening reactions of lactones lead to the same type of polyesters. Another type of polyesters with different characteristics is usually produced through condensation of dicarboxylic or polycarboxylic acids with di- or polyhydric alcohols.



Organic esters are of considerable economic importance. Esters of glycerol with fatty acids

(glycerides) occur naturally in large quantities in fats and fatty oils (see Chap. 4 and → Fats and Fatty Oils); they are used predominantly in foods, but also as raw materials, especially in the production of surfactants (→ Surfactants; Detergents; Soaps; Fatty Acids; Fatty Alcohols).

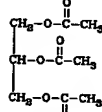
Cellulose acetate is used on a large scale in fiber production. Synthetic esters are of increasing importance in many applications, e.g., fibers, films, adhesives, and plastics articles. Various synthetic esters have been developed for specific uses, e.g., solvents, extractants, plasticizers, lubricants, lubricant additives, and lacquer bases (see also → Solvents; → Plasticizers). A variety of volatile esters are used as aromatic materials in perfumes, cosmetics, and foods (→ Flavors and Fragrances).

This article gives a general survey of production methods, properties, and uses of esters. The commercially most important esters are treated under separate keywords: → Formic Acid; Acetic Acid; Propionic Acid; Butyric Acid; Adipic Acid; Acrylic Acid and Derivatives; Methacrylic Acid and Methacrylates; Benzoic Acid; Phthalic Acid and Derivatives; Terephthalic Acid and Dimethyl Terephthalate; Fats and Fatty Oils; Waxes; Cellulose Esters; Polyesters; Polyvinyl Esters.

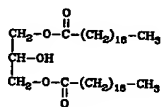
**Nomenclature.** The term ester was coined by GMELIN (1850) from the German word Essig-äther (acetic ether, ethyl acetate). According to IUPAC rule C-463, esters of carboxylic acids are named by substituting the ending -ate for the -ic acid; the alkyl or aryl group is cited first. For example, the methyl ester of propionic acid is called methyl propionate [1]. Alternatively, the term propionic acid methyl ester is used.

Acid esters, such as the monoesters of dibasic acids, are named by inserting the word hydrogen between the names of the alcohol and acid (IUPAC rule C-463.2). Thus, methyl hydrogen succinate is the monomethyl ester of succinic acid.

Esters of glycerol such as fats and fatty oils are known as glycerides. Trivial names are usually preferred:



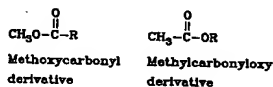
Triacetin



1,3-Distearin

Ortho esters are named as derivatives of ortho acids, e.g., trimethyl orthoacetate (IUPAC rule C-464).

In substitutive nomenclature, different prefixes are used for the ester group, depending on the position of the principal group R:



## 2. Physical Properties

The physical properties of commercially important aliphatic and aromatic esters are listed in Table 1 [2]. The lower esters are colorless, mobile, and highly volatile liquids that usually have pleasant odors. As the molecular mass increases, volatility decreases and the consistency becomes waxy, then solid, and eventually even brittle, often with formation of lustrous crystals.

The melting point of an ester is generally lower than that of the corresponding carboxylic acid. The boiling point depends on the chain length of the alcohol component and may eventually exceed that of the acid. The lower esters are relatively stable when dry and can be distilled without decomposition.

With the exception of low molecular mass compounds formed by short-chain carboxylic acids, esters are insoluble in water (Table 2). By contrast, they are readily miscible with many organic solvents.

## 3. Chemical Properties

Due to the large number of possible acid and alcohol moieties, the chemical properties of esters may differ considerably. Only typical reactions applicable to the majority of esters are described in the following sections.

### 3.1. Hydrolysis

Esters are gradually split into the acid and alcohol through the action of humidity:

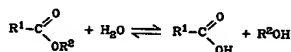


Table 1. Physical properties of the most important esters

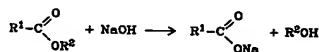
	CAS registry number	$M_r$	$n_D^{20}$ (DIN 51 423)	$d_4^{20}$ (DIN 51 757), g/cm <sup>3</sup>	$b_p$ at 101.3 kPa (DIN 53 171), °C	$f_p$ or $m_p$ , °C
<i>Esters of aliphatic acids</i>						
Methyl formate	[107-31-3]	60.05	1.344	0.975	32.0	-99.8
Ethyl formate	[109-94-4]	74.08	1.3598	0.924	54.3	-80
Methyl acetate	[79-20-9]	74.08	1.3594	0.933	57	-98.1
Ethyl acetate	[141-78-6]	88.10	1.3723	0.900	77.06	-83.6
Propyl acetate	[109-60-4]	102.13	1.3844	0.887	101.6	-92.5
Isopropyl acetate	[108-21-4]	102.13	1.3773	0.872	90	-73.4
Butyl acetate	[123-86-4]	116.16	1.3951	0.882	126	-73.5
Isobutyl acetate	[110-19-0]	116.16	1.3902	0.871	117.2	-98.6
Pentyl acetate	[628-63-7]	130.18	1.4023	0.876	149.25	-70.8
2-Ethylhexyl acetate	[103-09-3]	172.26	1.4204	0.873	199.3	-93
Vinyl acetate	[108-05-4]	86.10	1.3959	0.932	72.2-72.3	-93.2
Ethylene glycol diacetate	[111-55-7]	146.15	1.415	1.128 <sup>a</sup>	191	-31
Methoxyethyl acetate	[110-49-6]	118.13	1.4019	1.0067	145.0	-65.1
2-Ethoxyethyl acetate	[111-15-9]	132.16	1.4058	0.975	156.4	-61.7
2-Butoxyethyl acetate	[112-07-2]	160.21		0.943	187.8	-25
2-(2-Ethoxyethoxy)ethyl acetate	[111-90-0]	176.21		1.011	217.4	-32.2
2-(2-Butoxyethoxy)ethyl acetate	[112-34-5]	204.27		0.981	247	-51.5
Benzyl acetate	[140-11-4]	148.15	1.5232	1.055	215.5	-78
Glyceryl triacetate	[102-76-1]	218.23		1.161	258	-87.5
Methyl propionate	[554-12-1]	88.10	1.3775	0.915	79.8	-72.6
Ethyl propionate	[105-37-3]	102.13	1.3839	0.892	99.10	-80.7
Glyceryl tripropionate	[139-45-7]	260.3	1.4318	1.100	175-176 (2.67 kPa)	-80.7
Methyl butyrate	[623-42-7]	102.13	1.3878	0.898	102.3	-84.8
Ethyl butyrate	[105-54-4]	116.16	1.4000	0.878	121.6	-100.8
Butyl butyrate	[109-21-7]	144.22	1.4075	0.871	166.6	-91.5
Methyl isobutyrate	[547-63-7]	102.13	1.3840	0.891	92.6	-84.7
Ethyl isobutyrate	[97-62-1]	116.16	1.3903	0.870	110-111	-88
Isobutyl isobutyrate	[97-85-8]	144.22	1.3999	0.875	148.7	-80.7
Dimethyl adipate	[627-93-0]	174.20	1.4283	1.060	115 (1.73 kPa)	10.3
Diethyl adipate	[141-28-6]	202.25	1.4372	1.008	245	-19.8
Bis(2-ethylhexyl) adipate	[103-23-1]	370.58		0.927	214 (0.67 kPa)	-60
Methyl stearate	[112-61-8]	298.50	1.457 <sup>40</sup>	0.836 <sup>60</sup>	215 (2.0 kPa)	40
Ethyl stearate	[111-61-5]	312.52	1.429 <sup>40</sup>	0.848 <sup>36</sup>	213-215 (2.0 kPa)	33.7
Butyl stearate	[123-95-5]	340.58		0.855	343	27.5
Dodecyl stearate	[5303-25-3]	440.80	1.433 <sup>50</sup>			28
Hexadecyl stearate	[1190-63-2]	496.9	1.441 <sup>70</sup>			57
Methyl acrylate	[96-33-3]	86.09	1.4040	0.953	80.5	< -75
Ethyl acrylate	[140-88-5]	100.11	1.4068	0.923	99.8	< -72
Butyl acrylate	[141-32-2]	128.17	1.4185	0.898	69 (6.7 kPa)	-64.6
2-Ethylhexyl acrylate	[103-11-7]	184.28		0.887	130 (6.7 kPa)	-90
Methyl methacrylate	[80-62-6]	100.13	1.4119 <sup>25</sup>	0.944	100-101	-48
<i>Esters of aromatic acids</i>						
Methyl benzoate	[93-58-3]	136.14		1.094 <sup>15</sup>	199.5	-12.5
Ethyl benzoate	[93-89-0]	150.17		1.051 <sup>15</sup>	212.9	-34.2
Methyl salicylate	[119-36-8]	152.14		1.184 <sup>15</sup>	223.3	-8.6
Ethyl salicylate	[118-61-6]	166.17		1.137 <sup>15</sup>	231.5	1.3
Phenyl salicylate	[118-55-8]	214.21			172.3 (1.6 kPa)	43
Dimethyl phthalate	[131-11-3]	194.19			282	0-2
Diethyl phthalate	[84-66-2]	222.23	1.4990	1.118	295	-33
Bis(2-ethylhexyl)phthalate	[117-81-7]	390.57		0.986	231 (0.66 kPa)	-46
Dimethyl isophthalate	[1459-93-4]	194.18			124 (1.6 kPa)	67-68
Dimethyl terephthalate	[120-61-6]	194.18			288	14
Trimethyl trimellitate	[2459-10-1]	252.30			194 (1.6 kPa)	-13
Methyl anthranilate	[134-20-3]	151.16	1.584	1.168	132 (1.86 kPa)	24-25
Benzyl cinnamate	[103-41-3]	238.27			240-244 (3.3 kPa)	39

Table 2. Water solubility of lower esters

	CAS registry number	Solubility, g in 100 g of water	Temperature, °C
Methyl formate	[107-31-3]	21.3	20
Ethyl formate	[109-94-4]	11.0	18
Propyl formate	[110-74-7]	2.2	22
Butyl formate	[592-84-7]	1.0	22
Methyl acetate	[79-20-9]	25	20
Ethyl acetate	[141-78-6]	7.7	20
Propyl acetate	[109-60-4]	1.5	16
Isobutyl acetate	[110-19-0]	0.8	20
Butyl acetate	[123-86-4]	0.7	20
Methyl propionate	[554-12-1]	6.3	20
Ethyl propionate	[105-37-3]	1.7	20
Methyl butyrate	[623-42-7]	1.6	21
Ethyl butyrate	[105-54-4]	0.6	22
Methyl acetoacetate	[105-45-3]	40	20
Ethyl acetoacetate	[141-97-9]	9	20

This hydrolysis is catalyzed by acids (protons) or bases (hydroxyl ions). The catalytic effect of bases is generally stronger. Industrially, the hydrolysis of esters is usually carried out with bases. However, acid hydrolysis is preferred for the production of pure acids and for alkali-sensitive compounds.

Hydrolysis of esters by use of water and a mineral acid leads to an equilibrium mixture of ester, alcohol, and free carboxylic acid. If bases are used, the salt of the carboxylic acid is formed; the carboxylic acid is thus removed from the equilibrium and the reaction becomes irreversible:



Higher temperatures accelerate the reaction. Table 3 gives the relative rates of hydrolysis for some esters: hydrolysis is hindered by bulky acyl or alcohol groups, whereas acidifying groups increase the reaction rate.

Esters of secondary alcohols are hydrolyzed more slowly than those of primary alcohols. Esters of tertiary alcohols, e.g., *tert*-butyl esters, are exceptional in that they are readily hydrolyzed in the presence of acids and then often yield  $\alpha$ -olefins instead of alcohols. Some esters are hydrolyzed only under extreme conditions; for example, esters of pivalic acid [75-98-9] (2,2-dimethylpropionic acid) and ortho-substituted benzoic acids react only in concentrated  $\text{H}_2\text{SO}_4$ .

Table 3. Relative rates of acid-catalyzed hydrolysis of esters

	CAS registry number	$k_{\text{ester}}/k_{\text{CH}_3\text{COOC}_2\text{H}_5}$
$\text{CH}_3\text{COOC}_2\text{H}_5$	[141-78-6]	1
$\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$	[105-37-3]	0.47
$(\text{CH}_3)_2\text{CHCOOC}_2\text{H}_5$	[97-62-1]	0.10
$(\text{CH}_3)_3\text{CCOOC}_2\text{H}_5$	[3938-95-2]	0.01
$\text{CH}_3\text{COOCH}_2\text{CH}(\text{CH}_3)_2$	[110-19-0]	0.70
$\text{CH}_3\text{COOCH}_2\text{C}(\text{CH}_3)_3$	[926-41-0]	0.18
$\text{CH}_3\text{COOCH}_2\text{C}(\text{C}_6\text{H}_5)_3$	[10332-40-8]	0.03
$\text{CH}_3\text{COOCH}_3$	[79-20-9]	1.6
$(\text{COOCH}_3)_2$	[553-90-2]	284
$\text{CH}_2\text{ClCOOCH}_3$	[96-34-4]	1270
$\text{CHCl}_2\text{COOCH}_3$	[116-54-1]	27000
$\text{CH}_3\text{COCOOC}_2\text{H}_5$	[617-35-6]	17000

**Basic Hydrolysis.** Basic hydrolysis (saponification) is one of the earliest known chemical reactions. By this method, soaps are obtained from natural fats and oils, with glycerol as a byproduct. Saponification based on wood ash as the alkali was described as early as 2500 bc; the principle is still employed today ( $\rightarrow$  Soaps). The reaction was investigated by SCHEELE in 1779.

Basic hydrolysis requires stoichiometric amounts of alkali. The reaction is carried out by boiling the ester in an aqueous alkaline solution. Under these conditions, the alkali salt of the carboxylic acid is dissolved.

**Acidic Hydrolysis.** If the goal is to obtain free carboxylic acids rather than soaps, acid hydro-



lysis is the preferred method. Free acids are needed for various industrial purposes ( $\rightarrow$  Carboxylic Acids, Aliphatic;  $\rightarrow$  Fatty Acids). Complete hydrolysis can only be achieved by removal of the alcohol from the equilibrium. The reaction rate in dilute acids is generally fairly low, mainly because of the poor solubility of esters in water. Therefore, in practice, emulsifiers such as sulfonated oleic acid or sulfonated aromatic compounds (Twitchell reagent) are added and the reaction is carried out at ca. 100 °C under pressure.

Another industrial process involves high-temperature hydrolysis with steam at 170–300 °C under pressure. Zinc, calcium, and magnesium compounds are used as catalysts [3]. Vinyl esters are readily hydrolyzed in the presence of palladium salts [4].

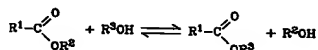
**Enzymatic Hydrolysis.** Specific lipolytic enzymes, the so-called esterases, effect hydrolysis at temperatures below 40 °C. Thus, lipase occurs in the digestive tracts of humans and most animals and in plants. Castor oil lipase is of commercial importance in hydrolysis of fats under mild conditions. The enzymes are especially effective in the weakly acidic range. Lipases may achieve importance as detergent additives; at low temperatures (20 °C) they facilitate the removal of fat-containing soils ( $\rightarrow$  Detergents, A8, p. 363).

### 3.2. Transesterification

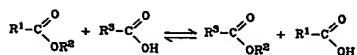
When esters are heated with alcohols, acids, or other esters, the alcohol or acid groups are exchanged more or less completely. This process is called transesterification. It is accelerated in the presence of a small amount of acid or alkali.

Three types of transesterification are known:

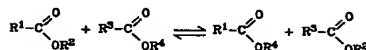
- 1) Exchange of alcohol groups (alcoholysis)



- 2) Exchange of acid groups (acidolysis)



- 3) Ester-ester interchange



All three are equilibrium reactions and proceed to completion only if one component is removed from the reaction mixture.

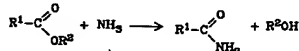
Dispersed alkali metals, mainly sodium, are suitable catalysts for the transesterification of fats [5]. Tin salts have been used in the production of aryl esters, e.g., phenyl esters, at 190–250 °C. Methacrylic acid esters of higher alcohols, e.g., ethylhexanol, can be obtained by transesterification in the presence of tin compounds [6] or with magnesium alkoxides [7]. Other catalysts are discussed in Section 5.5.

Transesterification reactions play a major role in industry and are important in laboratory practice and in analytical chemistry. They can be used to reduce the boiling point of esters by exchanging a long-chain alcohol group for a short one such as methanol, e.g., in the analysis of fats, oils, and waxes (see Chap. 7) and in vapor-phase reactions. Transesterification reactions can also be useful if direct esterification with the desired alcohol is technically difficult because of physical reasons (e.g., high boiling point, low solubility, or high viscosity). Examples are to be found in polymer chemistry. Thus, poly(ethylene terephthalate) is produced mainly by transesterification of dimethyl terephthalate with ethylene glycol. Propanediols and 1,4-butanediol are used in a similar manner. The reaction is catalyzed with calcium, antimony, titanium, and germanium salts. A further example is the reaction of diols (e.g., bisphenol A) with carbonic acid esters to produce polycarbonates.

An industrial example of acidolysis is the reaction of poly(vinyl acetate) with butyric acid to form poly(vinyl butyrate). Often a butyric acid-methanol mixture is used and methyl acetate is obtained as a coproduct.

### 3.3. Ammonolysis

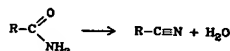
Ammonia and esters react to form alcohols and amides:



This reaction is similar to hydrolysis. It is carried out in aqueous or alcoholic ammonia. Lower esters give good yields even at room temperature; higher esters require higher temperature and pressure.

If primary or secondary amines are used, N-substituted amides are formed. This reaction is called aminolysis. Hydrazines yield the corresponding hydrazides.

If esters are passed with ammonia over a catalyst such as alumina at 400–500 °C, dehydration of the intermediate amides occurs and the corresponding nitriles are obtained directly.



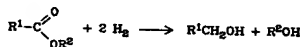
Fatty nitriles can be produced in this manner [8] (see also → Amines, Aliphatic, A 2, p. 21).

### 3.4. Reduction

Under certain conditions esters can be reduced to alcohols.

**Bouveault–Blanc Reduction.** This classical method developed in 1904 uses metallic sodium in alcohol (→ Fatty Alcohols). However, the Bouveault–Blanc reduction has been replaced nearly completely by catalytic hydrogenation and remains important only for laboratory purposes. The advantage of the Bouveault–Blanc process is that only the ester group is hydrogenated, while carbon–carbon double bonds are not reduced. Therefore, the reaction is suitable for the synthesis of unsaturated alcohols such as oleyl alcohol from unsaturated esters.

**Catalytic Hydrogenation.** A process of great industrial importance is the catalytic reduction of esters with hydrogen at 200–300 °C and 10–30 MPa (100–300 bar) in the presence of copper chromite catalysts [9]:

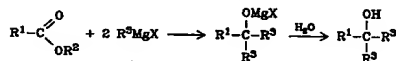


Sulfur and halogens are catalyst poisons. This method gives high yields and is used for the large-scale reduction of fats and fatty oils such as coconut oil and tallow, usually after transesterification to the methyl esters (→ Fatty Alcohols). The main products are dodecyl and decyl alcohols, which are important raw materials for the production of detergents. The method is also suitable for the conversion of 1,4-dimethyl terephthalate into 1,4-bis(hydroxymethyl) cyclo-

hexane [105-08-8], an important intermediate in the production of polyesters.

Hardening of fats (hydrogenation of double bonds in unsaturated fats and oils) is carried out in the presence of nickel catalysts under slight hydrogen pressure and does not involve ester splitting.

**Grignard Reaction.** Esters react with alkylmagnesium halides under Grignard conditions. Formic acid esters give secondary alcohols; the other esters yield tertiary alcohols.

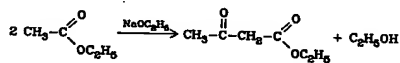


Yields are high, e.g., 95% in the production of triphenylmethanol from ethyl benzoate and phenylmagnesium bromide. The method is used mainly on a laboratory scale.

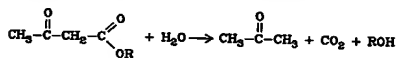
**Reduction with Complex Metal Hydrides.** The reduction of esters with complex metal hydrides, especially lithium aluminum hydride, has only preparative importance [10]. Its advantage is its broad applicability for all types of esters; double bonds are preserved. This method leads to very pure alcohols.

### 3.5. Claisen Condensation

The reaction of carboxylic acid esters with reactive methylene and methyl groups in the presence of alkaline compounds such as sodium alkoxides leads to the formation of  $\beta$ -oxocarboxylic acid esters ( $\beta$ -keto esters) [11]. The classical example is the condensation of two molecules of ethyl acetate to form acetoacetate:



Oxocarboxylic acid esters are among the most important intermediates in the laboratory and in industry. During hydrolysis with dilute alkali, these esters readily decompose into ketones, alcohols, and carbon dioxide:



Almost any ketone can be synthesized by using this process.

In industry, the Claisen condensation has been replaced by the synthesis of acetoacetic acid

derivatives from diketene [674-82-8], see also Section 5.6 ( $\rightarrow$  Oxocarboxylic Acids;  $\rightarrow$  Ketenes).

Condensation of esters in inert solvents in the presence of sodium rather than sodium ethoxide leads to formation of diketones and  $\alpha$ -hydroxy ketones (acyloins) [12]. This reaction is utilized in the synthesis of large-ring compounds.

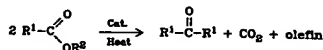
### 3.6. Pyrolysis

When passed at 300–500°C over an inert heat-transfer agent such as quartz glass, esters decompose into carboxylic acid and the unsaturated compound that corresponds to the alcohol. Esters of primary alcohols generally lead to  $\alpha$ -olefins:



The double bond does not migrate along the carbon chain. Methyl esters and other esters without hydrogen atoms in the  $\beta$ -position do not yield uniform pyrolysis products.

When heated to high temperatures in the presence of metal oxides such as thorium oxide, calcium oxide, manganese chromite, or zinc chromite, fatty acid esters or free fatty acids give high yields of ketones:



The alcohol moiety is split off as olefin.

## 4. Natural Sources

Esters occur naturally in large quantities in fats and fatty oils, waxes, and fruit ethers.

**Fats and Fatty Oils.** Fats and fatty oils (as opposed to mineral oils) are almost exclusively esters of glycerol with long- and medium-chain fatty acids. About 1300 different fats and oils are known. They contain mainly even-numbered, straight-chain carboxylic acids ( $\rightarrow$  Fats and Fatty Oils). The most common are the triglycerides of stearic, palmitic, and oleic acid. The melting point of the natural products varies between

55°C (mutton tallow) and –27°C (nut oil) and decreases as the content of unsaturated and short-chain fatty acids increases.

Only a few of the animal fats and vegetable oils are suitable for commercial production. They are predominantly used as foods, but have also gained considerable industrial importance, e.g., in the production of lacquers, detergents, and solvents. The most frequently produced fats of animal origin are butter, beef and mutton tallow, lard, fish oil, and whale oil. Butter accounts for ca. 40% of the world production of animal fats. The most important oils of plant origin are soybean oil, sunflowerseed oil, peanut oil, cottonseed oil, coconut oil, rapeseed oil, palm oil, and olive oil. Linseed oil, hempseed oil, and poppyseed oil contain a variable amount of unsaturated fatty acids, e.g., linoleic acid, linolenic acid, ricinoleic acid, and erucic acid. These oils gradually harden under the influence of oxygen in the air ( $\rightarrow$  Drying Oils).

**Waxes.** Natural waxes (wax esters) are esters of monobasic carboxylic acids with higher monohydric and, less commonly, dihydric alcohols. Currently they are largely replaced by synthetic waxes, which are in most cases long-chain hydrocarbons, but not esters ( $\rightarrow$  Waxes).

The most important sources of wax esters are beeswax, whose main constituent is myricyl palmitate [6027-71-0]; spermaceti from the head oil of the sperm whale, which contains cetyl palmitate [540-10-3]; and carnauba wax from the Brazilian palm, containing myricyl cerotate [84324-99-2]. Fossil waxes, such as montan waxes in bituminous lignite and peat waxes, also have major wax ester components. Lanolin, the neutral part of wool grease, contains higher fatty acid esters of cholesterol.

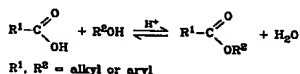
**Fruit Ethers.** Fruit ethers, i.e., volatile esters of short- and medium-chain carboxylic acids with short- and medium-chain alcohols, are major constituents of essential oils. Their name derives from their pleasant, usually fruity odor. They are used as aromatic materials in fragrances, foods, beverages, cosmetics, and soaps ( $\rightarrow$  Flavors and Fragrances). Natural fruit ethers are obtained from plant materials by extraction, steam distillation, pressing, or a combination of these methods. The majority of simple, short-chain esters are currently produced synthetically.

## 5. Production

A great variety of production methods for carboxylic acid esters are known. However, many of these methods are valuable only for preparing special compounds [13]. In what follows, only those methods that have industrial significance are discussed.

### 5.1. Esterification of Carboxylic Acids

The simplest and most common method of esterification is the reaction of a concentrated alcohol with a concentrated carboxylic acid with the elimination of water:



Esterification is the reverse of hydrolysis and leads to an equilibrium (see Section 3.1). With acetic acid and ethanol, the molar equilibrium ratio of ethyl acetate to acetic acid is ca. 2:1 (65 mol % of ethyl acetate). The equilibrium may be shifted toward the ester by increasing the concentration of one of the reactants, usually the alcohol. However, quantitative esterification is possible only by continuous removal of one of the products, i.e., ester or water. Usually the water is distilled off as an azeotrope (see Section 5.1.2).

Removal of the water by chemical or adsorptive binding is also possible. In preparative chemistry, calcium carbide, calcium hydride, and calcium and magnesium sulfate have proved successful; in industrial applications, activated bauxite is also used. The distilled, water-rich condensates are passed over the water-binding agents; alternatively, salts such as copper sulfate or calcium chloride can be added directly to the reaction mixture. Molecular sieves are also suitable [14]. Acetone dimethyl acetal, which binds water and simultaneously supplies methyl groups, may be used for the production of methyl esters [15].

Esterification is carried out at high temperature and in the presence of catalysts. The rate of ester formation depends on the carboxylic acid and the alcohol used. The lowest members, i.e., methanol and formic acid, react the most readily. Primary alcohols react faster than secondary alcohols, and the latter react faster than tertiary ones. Within each series, the reaction rate generally decreases with increasing molecular mass. Straight-chain acids react more readily than branched ones; the rate of esterification is

lowered particularly by branching in the  $\alpha$ -position. The relative rates of esterification are similar to those of hydrolysis (see Table 3). Esterification of aromatic acids, e.g., benzoic acid, is slow.

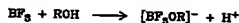
Experiments with primary and secondary alcohols containing  $^{18}\text{O}$  have shown that the oxygen in the water formed during acid-catalyzed esterification originates from the acid, not the alcohol [16]. The reaction of tertiary alcohols is more complex and does not proceed clearly via a tertiary carbonium ion. The mechanism is discussed in [17].

#### 5.1.1. Catalysts

**Mineral Acids.** Only strong carboxylic acids react sufficiently quickly without a catalyst. Generally, a strong mineral acid must be added. Suitable catalysts include sulfuric acid, hydrogen chloride, arylsulfonic acids such as *p*-toluenesulfonic acid, and chlorosulfuric acid. Phosphoric acid, polyphosphoric acids, and mixtures of acids are also recommended [18]. If the acids are adsorbed on a solid support, esterification can be carried out as a continuous process.

**Ion Exchangers.** The acid groups can be bound chemically to a polymeric material. Cation exchangers such as sulfonated polystyrene permit esterification under mild reaction conditions. The resulting esters are generally very pure because acid-catalyzed side reactions such as dehydration, etherification, and rearrangement are almost completely suppressed [19], [20]. This method gives high yields and is widely used in industry. After the reaction water has been removed, the ion exchanger is filtered off and the ester is purified by distillation. Zeolites are also used as esterification catalysts [21].

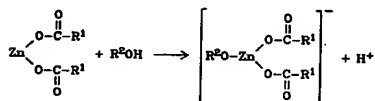
**Lewis Acids.** Lewis acids such as boron trifluoride increase the reactivity of the carboxyl group toward alcohols. Boron trifluoride reacts with alcohols under proton release:



The proton acts as a catalyst. The complex with diethyl ether, boron trifluoride etherate [109-63-7], is generally preferred because it is easier to handle than gaseous boron trifluoride [22]. This method of esterification proceeds under mild conditions and is widely applicable.

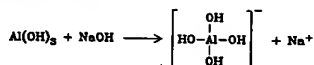
However, it is limited to the manufacture of high-value esters because of the relatively high price of  $\text{BF}_3$ . Each carboxyl group requires one equivalent of the boron trifluoride complex, which in most cases is destroyed during the further processing of the ester. All other groups that possess a free electron pair (e.g., hydroxyl, oxo, or amino groups) require an additional equivalent of  $\text{BF}_3$ .

Metal salts may also function as Lewis acids. For example, a complex acid is formed from the reaction of a zinc salt and an alcohol:



The actual catalysts are again the protons. Tin compounds have been used to prepare glyceryl esters. For the production of dimethyl terephthalate, silica treated with aluminum, titanium, zinc, or tin compounds has proved successful [23]; this esterification proceeds also in the absence of catalysts (12.5–14.0 MPa, 270–275 °C, 95% yield).

**Amphoteric Hydroxides.** Esterification is catalyzed by amphoteric hydroxides of metals of groups I, II, III, and IV, especially aluminum hydroxide. The actual catalyst is probably the aluminate anion:



The aluminate may be generated in the reaction mixture from aluminum hydroxide and sodium hydroxide [24]. The esters produced by this method are light in color, and purification by distillation is generally unnecessary. Therefore, this process is especially suitable for preparing esters with high boiling points. Its main application is in the production of plasticizers, e.g., phthalates.

**Other Compounds.** A possible esterification catalyst is graphite hydrogen sulfate [12689-13-3],  $(\text{C}_{24}\text{HSO}_4 \cdot 2\text{H}_2\text{SO}_4)_{17}$ . It is obtained by electrolysis of 98% sulfuric acid with a graphite anode.

Silanes and phosphoric acid derivatives are utilized for syntheses under mild conditions, the latter especially for phenyl carboxylates.

Acid esterification of amino acids and peptides is difficult because protecting groups and peptide bonds are easily hydrolyzed. High yields of esters of both protected and free

amino acids or peptides are obtained in the presence of a mild dehydration catalyst such as sulfonyl chloride or thionyl chloride at room temperature [25].

Trifluoroacetic anhydride is a suitable catalyst for the esterification of sterically hindered acids [26].

### 5.1.2. Industrial Processes

Esterification is generally carried out by refluxing the reaction mixture until all the water has been split off. The water or the ester is removed from the equilibrium by distillation. The choice of method to achieve complete esterification depends on the boiling points of the alcohol, the acid, and the ester.

Basically, the following three possibilities exist:

1) The boiling point of the ester is lower than that of water. In this case the ester can be distilled off together with the alcohol. This method is used to produce methyl acetate, which forms an azeotrope with methanol.

2) Ester and water can be distilled off together, usually as an azeotropic mixture. On condensation, the mixture separates into an ester and a water phase. To achieve complete distillation of the ester, water or steam are often added to the reaction mixture. An example of this method is the production of *sec*-butyl acetate. Frequently alcohol, ester, and water form ternary azeotropes, e.g., during the esterification of acetic acid with ethanol.

3) The boiling point of the ester is higher than that of water. In this case, the water is distilled off, frequently as an azeotrope with the alcohol. Except for methanol, all alcohols of medium volatility form azeotropes with water. If the alcohol–water mixture separates into two phases during condensation, the alcohol can be recycled into the reaction mixture, as exemplified in the production of *n*-dibutyl phthalate. If water and alcohol do not separate, fresh alcohol must be continuously introduced into the reaction mixture.

Removal of water usually involves the addition of entrainers, which form azeotropes with relatively low boiling points and high water content. Table 4 lists some frequently used entrainers. After condensation, the azeotrope separates into an aqueous phase and an organic phase, and the entrainer is recycled into the reaction mixture.

With ethanol, *n*-propanol, 2-propanol, allyl alcohol, and *tert*-butyl alcohol, a cosolvent such

Table 4. Composition of common azeotropes

Entrainer	bp, °C		Water content, wt %
	Entrainer	Azeotrope	
Benzene	80.2	69.2	8.8
Toluene	110.7	84.1	13.5
Xylene	139	92	35.8
Cyclohexane	80.7	68.9	9.0
Tetrachloromethane	76.7	66.0	4.1

as benzene or toluene is often added to the condensate to achieve separation of the organic phase [27].

With high-boiling esters, e.g., esters of polyhydric alcohols, the water of reaction may be removed by means of steam or inert gases. Steam distillation can also be used to remove excess alcohol after the esterification is complete.

Esterification is usually carried out batchwise. In commercial production, continuous processes are preferred. Special procedures have been devised in some cases.

Methyl and ethyl esters of mono- and dicarboxylic acids are produced continuously by pumping the alcohol and the carboxylic acid melt (e.g., lauric acid or adipic acid) into a pipe from below and drawing off the ester at the top [28]. In a continuous process for the production of volatile esters, the mixture of acid, alcohol, and catalyst is introduced into the upper part of a distillation column and an excess of the alcohol is introduced into the bottom. The column is heated so that the ester, water, and excess alcohol are distilled off [29].

Nonvolatile esters such as bis(2-ethylhexyl) phthalate [17-31-7] can be obtained continuously by the following procedure:

The mixture of acid or anhydride and alcohol together with sulfuric acid is introduced at the top of a plate column. An entrainer, e.g., benzene, is distilled through the column from below. The azeotrope of water and entrainer is drawn off the top and the ester accumulates in the sump.

Monochloroacetic acid esters of alcohols with three to five carbon atoms are obtained continuously by adding equimolar amounts of chloroacetic acid and alcohol to a chloroacetic acid melt and distilling off the ester and water.

Esterification can also be carried out continuously in the vapor phase by heating a mixture of acid, alcohol, ester, and catalyst to the reaction temperature. This process is called gas-phase esterification although one or more of the components may be present as liquids or solids.

Ion-exchange resins are especially suitable as catalysts in continuous processes. The reactants pass through or over the solid catalyst, and no separation or neutralization of the catalyst is necessary [20].

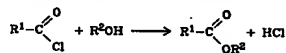
## 5.2. Alkylation of Metal Carboxylates

If metal carboxylates are treated with alkylating agents, good yields of carboxylic acid esters result. A one-pot procedure is often used, in which the salt is first produced from the carboxylic acid and then directly alkylated to form the ester. Isolation of the salt is necessary only in the case of thermally unstable quaternary ammonium salts [30].

Alkali metal and alkaline-earth metal salts, as well as silver and copper salts, can be used. Dialkyl sulfates, aliphatic halides such as long-chain alkyl chlorides, and alicyclic halides are suitable alkylating agents. The method is used mainly in preparative chemistry.

## 5.3. Acylation with Acyl Halides

High yields of esters are obtained by acylation of alcohols with carboxylic acid halides:



The acyl chloride is often produced in situ. The liberated hydrogen halide is generally bound to a base, e.g., pyridine or alkali hydroxide (Schotten-Baumann reaction).

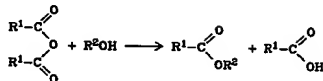
This method is particularly important in preparative and analytical chemistry. A commercial application is the production of polycarbonates from phosgene and diols. Phenyl esters and esters of sterically hindered carboxylic acids can be produced from the corresponding acyl halides in the presence of Lewis acids, e.g., iron(III), aluminum, tin(IV), and titanium(IV) chlorides. Addition of phase-transfer agents such as tetrabutylammonium chloride has also proved effective [31]. An important application of this method is in the esterification of steroids.

## 5.4. Acylation with Carboxylic Anhydrides

Carboxylic anhydrides are suitable acylating agents for alcohols and phenols. With the exception of trifluoroacetic anhydride and mixed carboxylic anhydrides, they are less reactive than acyl halides.

The advantage of this method is that no water is formed; however, only one equivalent acyl

per molecule of anhydride is available for esterification:



Therefore, the method is especially suitable for the esterification of rare or expensive alcohols with cheap anhydrides such as acetic anhydride.

Acylation can be accelerated by addition of protonic acids (sulfuric acid, hydrochloric acid, perchloric acid, *p*-toluenesulfonic acid) or Lewis acids (zinc chloride). A large-scale commercial process is the production of cellulose acetate from cellulose and acetic anhydride ( $\rightarrow$  Cellulose Esters, A5, pp. 438–443).

Another important product is acetylsalicylic acid (aspirin), which is obtained from salicylic acid and acetic anhydride.

Base-catalyzed acylation with anhydrides is used to synthesize esters from sterically hindered or acid-sensitive alcohols [32], [33]. Common bases are triethylamine and pyridine.

Reaction with anhydrides is the basis of a quantitative analytical method for hydroxyl groups.

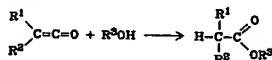
### 5.5. Transesterification

This method has already been described in Section 3.2. Transesterifications take place under extremely mild conditions, which permits the reaction of components containing additional functional groups. Chiral centers can be preserved in many cases.

The most common transesterification catalysts are protonic acids (sulfuric acid, perchloric acid, *p*-toluenesulfonic acid, and molecular sieves). Alkaline catalysts such as alkoxides or anionic ion exchangers are especially effective in peptide chemistry. Potassium cyanide is recommended for unsaturated esters, which undergo *cis*–*trans* isomerization in the presence of acids. Thallium(I) salts are also employed. If titanium(IV) alkoxides or complexes of triphenylphosphine with trialkyltin alkoxides or with copper alkoxides are used, the alkoxide component need not be identical with the alcohol group that is exchanged.

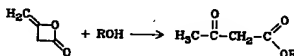
### 5.6. Acylation with Ketenes

Ketenes react with alcohols or phenols to form carboxylic acid esters:



The addition is catalyzed by acids and bases (e.g., pyridine or sodium acetate). The use of ketenes is limited because they are difficult to handle and equally good results can be achieved with other acylating agents such as acyl halides and anhydrides.

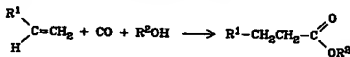
The alcoholysis of diketene is an important method for the commercial production of  $\beta$ -oxocarboxylic acid esters (acetoacetates), especially ethyl acetoacetate [141-97-9] [34]:



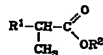
Acetoacetic acid anilides are produced in a similar way. These compounds are used in the synthesis of dyes, especially fast yellow dyes.

### 5.7. Carbonylation

The preparation of carboxylic acid esters by carbonylation of olefins in alcoholic solution (Rippe synthesis) is used on an industrial scale, e.g., in the production of methyl and ethyl propionate ( $\rightarrow$  Carbonylation) [35]:



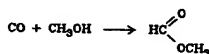
The linear ester is obtained in 85% yield, with less than 10% branched ester of the following structure:



The reaction is carried out at a moderate temperature (ca. 100°C) and a CO pressure of 20–25 MPa (200–250 bar). Iron, nickel, and cobalt salts, which are converted into the corresponding metal carbonyls during the reaction, and palladium or rhodium complexes are used as catalysts. A typical example is a bimetallic complex of bis(triphenylphosphine)palladium(II) chloride and tin(II) chloride [36]. Similarly, 1,3-dienes give  $\gamma,\delta$ -unsaturated esters.

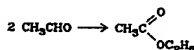
Alkyl, benzyl, vinyl, aryl, and allyl halides can also be carbonylated in the presence of suitable catalysts such as Mn-Fe-Ni powders. These reactions require only a low CO pressure [37].

Carbonylation of alcohols at a pressure up to 70 MPa (700 bar) in the absence of olefins gives formates. Thus, methyl formate is obtained by carbonylation of methanol at 70°C and 2–20 MPa (20–200 bar) in the presence of sodium methoxide [38]:



### 5.8. Condensation of Aldehydes

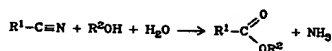
The condensation of two acetaldehyde molecules (Tishchenko reaction) is an important industrial process for the production of ethyl acetate:



Aluminum ethoxide promoted with chloride ions serves as a catalyst. In practice, acetaldehyde is passed at 0–5°C through a mixture of aluminum filings and traces of  $\text{AlCl}_3$  in ethanol-ethyl acetate; the yield is 95%.

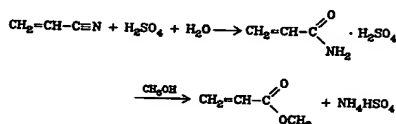
### 5.9. Alcoholysis of Nitriles

Nitriles react directly with alcohols to produce the corresponding esters:



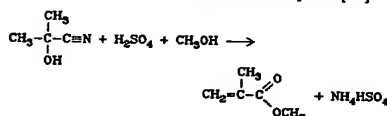
The ammonia that is formed must be removed from the equilibrium, preferably by using an excess of a strong mineral acid, e.g., sulfuric acid or *p*-toluenesulfonic acid. The acid also acts as a catalyst [39].

This method is used widely in industry for the production of esters from unsaturated nitriles such as acrylonitrile and methacrylonitrile. Alcoholysis of acrylonitrile is carried out with concentrated sulfuric acid. This leads initially to formation of the acrylamide sulfate, which then reacts with the alcohol (preferably methanol or ethanol) to produce the ester:



Selectivity for methyl acrylate is > 90%. A disadvantage of this process is the formation of ammonium hydrogen sulfate, which cannot be used economically. An alternative process, which avoids formation of this byproduct, is the vapor-phase alcoholysis of acrylonitrile in the presence of boric oxide [40].

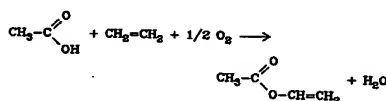
Methyl methacrylate is obtained by alcoholysis of the methacrylonitrile precursor acetone cyanohydrin. In this case, methacrylamide sulfate is first produced by using 98%  $\text{H}_2\text{SO}_4$  at 80–140°C, which is then reacted with methanol at 80°C to produce methyl methacrylate [41].



Selectivity based on acetone is 77%. Other methods, which avoid the formation of  $\text{NH}_4\text{HSO}_4$ , have been developed on a pilot-plant scale.

### 5.10. Acylation of Olefins

Direct addition of olefins to carboxylic acids is used on a large scale for the production of vinyl acetate, the ester of the hypothetical vinyl alcohol (→ Vinyl Esters).



The presence of stoichiometric amounts of oxygen or air is necessary. Palladium or palladium salts are essential as catalysts; other group VIII metals are less effective.

The process can be carried out in the vapor phase or in the liquid phase. Currently, only the vapor-phase process is used on an industrial scale. The reaction conditions are 175–200°C and 0.5–1 MPa (5–10 bar); the catalyst consists

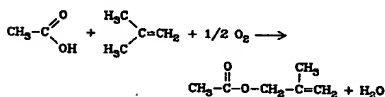


of palladium metal and alkali acetate on a carrier. The carrier is necessary for activation and higher selectivity. During the reaction, the alkali acetate is slowly removed from the catalyst and has to be continuously replaced [42]. The vapor-phase process avoids the corrosion problems of the liquid-phase process and gives better yields of vinyl acetate (94% based on ethylene or 98–99% based on acetic acid).

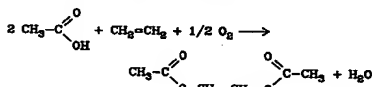
The liquid-phase process is no longer used on an industrial scale. This process is closely related to the Wacker–Hoechst acetaldehyde process ( $\rightarrow$  Acetaldehyde, A1, pp. 36–38). The catalyst contains copper salts as a redox system. The advantages of the liquid-phase process are a better control of the highly exothermic reaction and the generation of acetaldehyde as a byproduct, which can be oxidized to acetic acid. In this way the necessary acetic acid can be entirely produced from ethylene. The disadvantages are corrosion problems and a lower yield of vinyl acetate, based on ethylene.

The olefin process has replaced the older process based on acetic acid and acetylene, because ethylene is cheaper and more readily available in larger quantities.

Allyl esters are produced from propene, carboxylic acids, and oxygen by using a vapor-phase process. Supported catalysts impregnated with palladium salts and bismuth or cadmium compounds are used [43]. Methallyl acetate is obtained from isobutene and acetic acid in the presence of palladium(II) chloride [44]:



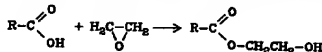
Glycol mono- and diesters can be produced from olefins and carboxylic acids by adding stoichiometric amounts of oxygen:



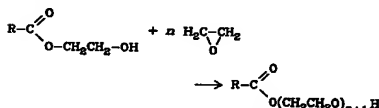
### 5.11. Ethoxylation of Carboxylic Acids

Addition of ethylene oxide to carboxylic acids generally proceeds smoothly and quickly. The low acidity of the carboxylic acids is suffi-

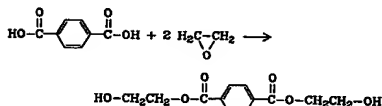
cient to split the strained three-membered ring; no catalyst is required in the first addition step:



Further ethoxylation yields polyglycol esters; this reaction can be controlled or entirely suppressed by addition of bases such as alkali or amines.



Ethoxylation reactions are widely used in industry. An example is the production of bis(2-hydroxyethyl) terephthalate [6422-86-2], by controlled ethoxylation of terephthalic acid:

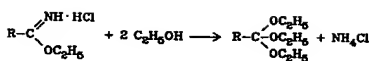


This ester is readily purified by crystallization from water, so that crude terephthalic acid can be used. The ethoxylation is carried out in the liquid phase at 2–3 MPa (20–30 bar) and 90–130 °C; no solvent is necessary. The presence of amines or quaternary alkylammonium salts is needed to avoid polyethoxylation. A considerable amount of poly(ethylene terephthalate) is produced by condensation of bis(2-hydroxyethyl) terephthalate.

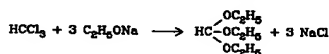
Polyethoxylation of aliphatic carboxylic acids also is an industrial process. It is carried out under pressure at 120–220 °C in the presence of sodium hydroxide or sodium acetate. Addition of 10–30 mol of ethylene oxide per mole of acid causes fatty acids such as stearic acid to lose their hydrophobicity. The products have many applications, e.g., as surfactants. The degree of hydrophilicity depends on the number of glycol units. Ethoxylation of short-chain carboxylic acids yields hydrophilic lubricating oils.

### 5.12. Orthocarboxylic Acid Esters

Free orthocarboxylic acids are unstable. Their esters can be prepared by reaction of imido ethers with alcohols:



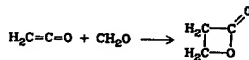
Orthoformic acid ethyl ester [122-51-0] is obtained from chloroform and sodium ethoxide:



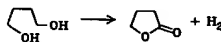
Orthoformates are relatively stable toward alkali; however, they are readily hydrolyzed by acids. In preparative chemistry, orthoformates are used to synthesize acetals and ketals. They also serve for the incorporation of methine groups into compounds with reactive methylene groups.

### 5.13. Lactones

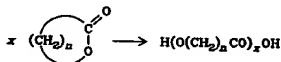
Lactones are internal esters of hydroxycarboxylic acids. Of commercial interest are  $\beta$ -propiolactone [57-57-8] and  $\gamma$ -butyrolactone [96-48-0].  $\beta$ -Propiolactone can be produced from ketene and formaldehyde in the presence of zinc chloride:



$\gamma$ -Butyrolactone is produced mainly by dehydrogenation of 1,4-butanediol ( $\rightarrow$  Butyrolactone, A4, p. 496):



Lactones with five- and six-membered rings ( $\gamma$ - and  $\delta$ -lactones) are the most stable. They readily form polyesters according to the following equation:



## 6. Environmental Protection

Most esters are synthesized by esterification of an acid with an alcohol, water being the only byproduct. Special environmental protection measures are usually unnecessary. Most esters possess low toxicity (Chap. 10). Because many of

Table 5. Biodegradation of organic esters

	Degree of degradation, %	BOD <sub>5</sub> **
Methyl acetate	> 95	ca. 500
Ethyl acetate	> 90	770
Vinyl acetate	> 90	810
Butyl acetate	> 95	1000
2-Methoxyethyl acetate	100	450
2-Butoxyethyl acetate	100	260
2-(2-Butoxyethoxy)ethyl acetate	100	380
Methyl acetoacetate	100	940
Ethyl acetoacetate	> 90	780
<i>n</i> -Butyl glycolate	93	570
Methyl crotonate	> 95	1050
Dimethyl acetylsuccinate	> 95	1100
Diethyl acetylsuccinate	> 95	1070
Dimethyl maleate	100	20
Monomethyl maleate	> 95	150
Diethyl maleate	> 90	200
Dibutyl maleate	99	630
Di(2-ethylhexyl)maleate	100	1450
Methyl 3-aminobenzoate	95	10
Methyl 4-hydroxybenzoate	100	1080
Methyl 4-hydroxyphenylacetate	98	320

\* According to DIN 38 412, Part 25.

\*\* Biochemical oxygen demand (milligrams of O<sub>2</sub> per liter of wastewater; sum over 5 d).

Table 6. Toxicity for fishes and bacteria [58]

	Fishes* LC <sub>50</sub> , mg/L	Bacteria** EC <sub>50</sub> , mg/L
Methyl acetate		1500
Ethyl acetate	135-310	2000
Vinyl acetate	9	400
Butyl acetate	44-70	1200
2-Methoxyethyl acetate	150	1000
2-Butoxyethyl acetate	25	800
2-Ethoxyethyl acetate	90-116	
3-Methoxybutyl acetate		> 2500
2-(2-Butoxyethoxy)ethyl acetate	100	1000-2000
Methyl acetoacetate	250	500
Ethyl acetoacetate	173-412	3000
<i>N</i> -Butyl glycolate	50	100
Methyl crotonate		1250
Butyl acrylate	9	80
Methyl dimethylacrylate		200
Dimethyl acetylsuccinate	100	1500
Diethyl acetylsuccinate	50	2500
Dimethyl maleate	25	100
Monomethyl maleate	50	600
Diethyl maleate	25	800
Dibutyl maleate	12	40
Di(2-ethylhexyl) maleate	40	20
Methyl 3-aminobenzoate	100	1000
Methyl 4-hydroxybenzoate	100	1000
Methyl 4-hydroxyphenyl acetate		400

\* DIN 38 412, Part 15.

\*\* Measurement of CO<sub>2</sub> evolution in fermentation of bacterial sludge; EC<sub>50</sub> is the concentration at which CO<sub>2</sub> evolution is not suppressed.

them are easily hydrolyzed on contact with water or moist air, the toxicological properties of the acid and alcohol component may need to be considered.

**Waste Gases.** Volatile esters with low carbon numbers are predominantly used as solvents and diluents for lacquers and plastics. Large-scale applications, e.g., in the auto and furniture industries, require excellent ventilation. The solvent vapors are suctioned off and burned in a flare or muffle furnace.

**Waste Liquors.** Short-chain esters and esters with hydrophilic groups are noticeably soluble in water; some results of biodegradability tests are listed in Table 5. The toxicity of some common esters for fishes and microorganisms is shown in Table 6.

## 7. Quality Specifications and Analysis

Table 7 shows some typical specifications of commercial products.

The most common analytical method is the determination of the saponification value, i.e., the number of milligrams of KOH necessary to hydrolyze 1.0 g of ester:

The ester (0.5–1 g) is refluxed for 30 min with 10 mL of 0.5 N alcoholic KOH. After cooling, the excess alkali is titrated with 0.5 N HCl using phenolphthalein as the indicator.

Before determination of the saponification value, determination of the free acid by titration with alkali in a water–alcohol mixture is often necessary.

The ester group can be readily identified by its characteristic absorption bands in the IR spectrum: the strong carbonyl absorption band at ca.  $1740\text{ cm}^{-1}$  and two C–O stretching bands between  $1300$  and  $1100\text{ cm}^{-1}$  [45].

Gas chromatography is suitable only for highly volatile esters. Esters with high boiling points must first be converted into low-boiling esters (usually methyl esters) either by transesterification or by quantitative hydrolysis and subsequent reesterification. Quantitative conversion into the methyl ester can be achieved with diazomethane, methyl iodide–calcium oxide in dimethyl sulfoxide (DMSO), or with the boron trifluoride–methanol complex [46].

Unsaturated esters, e.g., natural fats and oils, are often sufficiently characterized by their iodine value. This is defined as the number of grams of iodine bound by 100 g of an unsaturated ester and is a measure of the number of double bonds in the molecule.

An overview of the different analytical methods is given in [47]. Physical properties such as boiling range, melting point, density, refractive index, residue or ash content, and color are also used to identify esters or mixtures of esters. Previous separation of the different components, (e.g., by high-vacuum distillation) is often unnecessary.

## 8. Storage and Transportation

All organic esters are flammable. The flash points, autoignition temperatures, and flammable limits of representative commercial esters are given in Table 7. The ignition group according to the NFPA (National Fire Prevention Association) corresponds approximately to the danger class of the German VbF (Verordnung über brennbare Flüssigkeiten of 27. Feb. 1980).

If esters are stored in tanks, a nitrogen blanket and a carbon filter is necessary. In some cases, the ventilation pipe must be linked to a flare.

Mild steel, aluminum, or other metallic materials can be used for storage and transportation. Plastics are unsuitable because the highly lipophilic esters may migrate into the container walls and cause them to soften or even dissolve. Esters with a high melting point, such as waxes, can also be transported in paper sacks or wooden barrels.

## 9. Uses and Economic Aspects

**Solvents.** Because of their highly lipophilic and hydrophobic nature and low polarity, esters are widely used as solvents, extractants, and diluents [48], [49]. Lower esters, especially the acetates of methanol, ethanol, propanols, and butanols, are good solvents for cellulose nitrate and other cellulose derivatives. Ethyl acetate is the most common technical solvent. Branched esters and esters of ethylene glycol also have good solvent properties. Considerable quantities of esters are used as diluents in paints, lacquers,

Table 7. Typical specifications of commercial esters

	Color, max. *	$n_D^{20}$	$d_4^{20}$	Distillation range, °C (101.3 kPa)	Freezing point, °C	Flash point <sup>b</sup> , °C	Auto- ignition temper- ature, °C	Lower flammable limit, vol % in air (t, °C)	Evapo- ration number (diethyl ether = 1.0)	Ignition group <sup>c</sup>
Methyl acetate	10	1.3601	0.930	56-58	-13	-13	455	3.1	2.2	IA
Ethyl acetate	10	1.371-1.373	0.889	76-78	-84	-4	460	2.1(38)	2.9	IA
Propyl acetate	15	1.3844	0.885	99.0-103.0	-93	14	457	1.7(38)		IB
Isopropyl acetate	10	1.3772	0.872	85.0-90.0	-62	6	479	1.76(38)		IB
Butyl acetate	10	1.394	0.880	124-127	-74	25	422	1.38(38)	14	IC
Isobutyl acetate	10	1.390	0.870	119-118	-99	18	478	1.27(93)	8	
2-Ethylhexyl acetate	15	1.4103	0.872	192.0-205.0	-93	79	268	0.76(93)		IIIA
Vinyl acetate	5	1.369	0.93	72-74	-93	-8				IA
Ethylene glycol diacetate	15	1.4159	1.107	187.9-193.0	-42	99	482	1.6(135)		IIIA
2-Methoxyethyl acetate	20	1.4602	1.003	142-148	-61	44	400	1.7	34	II
2-Ethoxyethyl acetate	15	1.406	0.972	152-158	-61	51	392	1.24(93)	60	II
2-Butoxyethyl acetate	15	1.4200	0.94	186.0-194.0	-64	81	340	0.88(93)		IIIA
2-(2-Ethoxyethoxy)ethyl acetate	15	1.4230	1.011	214.0-221.0	-25	107	360	0.98(135)		IIIB
2-(2-Butoxyethoxy)ethyl acetate	15	1.4265	0.978	244-250	-32	116	290	0.76(135)	1200	IIIB
Glycerol triacetate	5	1.4296	1.160	258.0	3.2	153	432	1.05(189)		IIIB
Isobutyl isobutyrate	15	1.4314	1.09	285.0	-58	167	421	0.8(186)		IIIB
Bis(2-ethylhexyl)adipate	20	1.4472	0.855	144.0-151.0	-80	38	432	0.96(93)		II
Methyl acetoacetate	20	1.411	1.076	166-173	< -70	206	377	0.38(242)		IIIB
Ethyl acetoacetate	20	1.420	1.030	175-184	62	280	280	1.8	120	IIIA
Butyl glycolate	10	1.425	1.023	183-197	65	350	350	1	135	IIIA
Methyl acrylate	10		0.9568	79.8-80.3	75	404	404	0.6	460	IIIA
Ethyl acrylate	10		0.9235	98.8-99.8	10					IA
Butyl acrylate	10		0.9009	145.7-148.0	49					IA
2-Ethylhexyl acrylate	10		0.8862	214.8-218.0	91					II
Dimethyl phthalate	5	1.513	1.192	284	-1	157	490	0.94(181)		IIIA
Diethyl phthalate	10	1.4990	1.120	298	< -50	161	457	0.75(187)		IIIB
Dibutyl phthalate	15	1.4905	1.048	340	-35	190	404	0.47(236)		IIIB
Bis(2-ethylhexyl) phthalate	20-25	1.4856	0.9852	384	-50	216	391	0.28(246)		IIIB
Dimethyl terephthalate	< 15			288	140.6	153	519			IIIB
Bis(2-ethylhexyl) terephthalate	15	1.4867	0.9825	383	-48	238	399			IIIB
Bis(2-ethylhexyl) trimellitate	40	1.4832	0.989	600	-38	263	410	0.26	2.5	IIIB

\* Pt-Co scale. <sup>b</sup> According to ASTM D 56-52, similar to DIN 51 755 and 51 758. <sup>c</sup> ASTM D-2155, similar to DIN 51 794. <sup>d</sup> According to NFPA (National Fire Prevention Association).

Table 8. Production of miscellaneous esters in 1985, t

	CAS registry number	United States	Western Europe	Japan
Methyl acetate	[79-20-9]		17 350 *	
Ethyl acetate	[141-78-6]	87 270	ca. 100 000 *	117 388
Propyl acetate	[109-60-4]	27 700		
n-Butyl acetate	[123-86-4]	81 430	} ca. 50 000 *	29 942
Isobutyl acetate	[110-19-0]	34 880		
Vinyl acetate	[108-05-4]	960 200		
2-Ethoxyethyl acetate	[111-15-9]	46 840	> 200 000 *	402 930
Ethyl acetoacetate	[141-97-9]		19 450 *	
Acrylic acid esters, total			250 000	103 880
Butyl acrylate	[141-32-2]	192 560	88 000	33 000
Methyl acrylate	[96-33-3]	ca. 10 000	50 000	25 000
Ethyl acrylate	[140-88-5]	137 800	62 000	16 000
2-Ethylhexyl acrylate	[103-11-7]	36 020	50 000	29 000
Methyl methacrylate	[80-62-6]	390 060	ca. 200 000 *	236 690
Dibutyl maleate	[105-76-0]	1 540		
Dimethyl terephthalate	[120-61-6]	ca. 2 × 10 <sup>6</sup>	ca. 500 000 *	327 870

\* Federal Republic of Germany.

Table 9. Production of plasticizers in 1985, t

	CAS registry number	United States	Western Europe	Japan
Phthalic acid esters, total		516 350	960 000	356 910
Dibutyl phthalate	[84-74-2]	9 880	22 000 *	16 900
Diethyl phthalate	[84-66-2]	7 800		
Diisodecyl phthalate	[26761-40-0]	66 500	70 000	10 510
			39 850 *	
Dimethyl phthalate	[131-11-3]	3 480		
Diocetyl phthalate	[117-81-7]	125 180	525 000	240 720
			222 320 *	
Ditridecyl phthalate	[119-06-2]	9 910		
Trimellitic acid esters, total		22 070		
Other cyclic esters, total		23 060		
Adipic acid esters, total		56 900	28 000	23 740
Bis(2-ethylhexyl) adipate	[103-23-1]	16 870		13 000
Complex linear polyesters, total		22 510		11 260
Ethoxylated esters, total		51 130	37 000	17 900
Oleic esters, total		5 240		
Butyl oleate	[142-77-8]	760		
Palmitic acid esters		1 550		
Sebacic acid esters		1 650	7 000	
Stearic acid esters, total		4 500		
Butyl stearate	[123-95-5]	3 500		

\* Federal Republic of Germany.

and coatings. Methyl acetate is employed in fast-drying lacquers. Due to the development of low-solvent and solvent-free paints, e.g., for auto paints, the use of esters as diluents is decreasing. Table 8 gives production data for some acetates.

**Plasticizers.** Large quantities of esters, especially phthalates, adipates, and fatty acid esters, are used as plasticizers [50], [51]. Production data for some important plasticizers are listed in Table 9. Isooctanoic acid esters and 2-ethyl-

hexanoic acid esters of ethylene glycol are plasticizers for poly(vinyl chloride).

**Surfactants.** Natural fats, oils, and waxes are used in considerable quantities as raw materials in the production of soap (alkali salts of fatty acids) and other detergents and surfactants (Table 10). Hydroxyethyl esters of long-chain fatty acids are sold as nonionic surfactants (nonionics), which are easily biodegradable. About 34 100 t of ethoxylated natural fats and

Table 10. United States production of esters used as surfactants (1985)

	Production, t
Carboxylic acid esters, total	117 800
Anhydrosorbitol esters, total	15 320
Monostearate	8 080
Monooleate	3 080
Ethoxylated anhydrosorbitol esters, total	14 020
Monostearate	5 040
Monooleate	3 480
Glycerol esters, total	27 600
Monostearate	5 070
Monooleate	2 790
Glycerol esters of mixed acids	14 260
Diethylene glycol esters, total	8 900
Poly(ethylene glycol) esters, total	21 170
Monostearate	2 700
Monooleate	1 620
Monolaurate	2 290
Natural fats and oils, ethoxylated	15 000
Castor oil, ethoxylated	6 260

oils were produced in the Federal Republic of Germany in 1985, as compared to only 1380 t in Japan. A defined number of ethylene oxide molecules can be added to the fatty acid by varying the process conditions; compounds with a specific water solubility — from moderate to excellent — can thus be obtained. Nonionics are important as low-foaming detergents and as emulsifiers. They are also used in the food, textile, cosmetics, and pharmaceutical industries. Because of their heat and salt resistance, they are suitable as lubricants in deep-well drilling.

**Polyesters.** Higher esters derived from natural products, e.g., cellulose acetate and cellulose nitrate, are of considerable economic importance (→ Cellulose Esters). However, they are being gradually replaced by synthetic polyesters produced from monomers such as acrylates, terephthalates, and vinyl acetate (Table 8).

Vinyl acetate, with a worldwide production of  $2 \times 10^6$  t/a, is the most important aliphatic ester (→ Vinyl Esters). Poly(vinyl acetate) is produced in large quantities for use in plastics, coatings, adhesives, and laminates (→ Polyvinyl Esters). A considerable proportion is converted into poly(vinyl alcohol) [38]. Polymerization of acrylates such as methyl acrylate and methyl methacrylate yields homopolymers and mixed polymers used in paints, lacquers, and coatings. Polycondensation of dicarboxylic acids and diols gives polyester resins and plastics. Linear polyesters in particular are produced in large quantities.

Linear polyesters are used in the manufacture of synthetic fibers, packaging films, tapes, films for electric insulation, and a variety of plastics articles such as plastic bottles; they are also employed in hot-melt adhesives.

Polyesters are produced chiefly by transesterification. The most important raw material is dimethyl terephthalate. This undergoes polycondensation with a diol (e.g., 1,2-ethanediol, 1,2-propanediol, 1,4-butanediol, 1,4-cyclohexanedimethanol), and methanol is released. However, direct esterification of terephthalic acid with ethylene oxide and polymerization of the resulting bis(2-hydroxyethyl) terephthalate is also used (see Section 5.11). Copolymerization with unsaturated acids such as maleic acid yields polymers that can be cross-linked (thermosetting polymers).

Alkyd resins are an important group of polyesters used mainly in lacquers. The stability of the lacquer, e.g., its weatherability, can be improved by adding esters that are highly resistant to hydrolysis, such as pivalic acid esters.

**Flavors and Fragrances.** Certain esters with a pleasant odor are used in fragrances, flavors, cosmetics, and soaps. Production data for the most important flavor and perfume esters are given in Table 11. Although the quantities that are used are small, these esters are of great commercial importance because they are expensive [52]. Terpene esters as well as simple esters such as butyl and isobutyl acetate (fruity flavor) and benzyl acetate (jasmine odor) are widely used. These esters can be obtained from plant extracts, but many are currently produced by synthetic processes (→ Flavors and Fragrances).

Table 11. United States production of flavor and perfume esters (1985)

	CAS registry number	Production, t
Cedryl acetate	[77-54-3]	90
Geranyl acetate	[105-87-3]	60
Isoamyl acetate	[123-92-2]	51
Isoamyl butyrate	[106-27-4]	45
1,3-Nonanediol diacetate	[63270-14-4]	41
Citronellyl acetate	[150-84-5]	35
Benzyl propionate	[122-63-4]	20
2-Phenylethylphenyl acetate	[102-20-5]	15
Vetiveryl acetate	[117-98-6]	13
Isopentyl isovalerate	[639-70-1]	11
Allyl hexanoate	[123-68-2]	11
Neryl acetate	[141-12-8]	10
Citronellyl formate	[105-85-1]	9

Table 12. Toxicity data for various esters [53]-[57]

	LD <sub>50</sub> (rat, oral), g/kg	Inhalation (rat, 4-6 h)	TLV, ppm	mg/m <sup>3</sup>	Comments
Methyl formate	1.622 <sup>a</sup>	10 000 ppm: lethal <sup>f</sup>	100	250	
Methyl acetate	3.7 <sup>a</sup>	11 220: lethal <sup>f</sup>	200	610	irritation and burning of the eyes; narcotic; readily absorbed through the skin
Ethyl acetate	11.3	8 000 ppm: survival 16 000 ppm: lethal	400	1400	irritation of mucous membranes
Propyl acetate	> 3.2	5 300 ppm: survival	200	840	irritation of the eyes
Isopropyl acetate	3.0-6.5	32 000 ppm: lethal	250	950	irritation of eyes, nose, and throat; defeating of skin
n-Butyl acetate	> 6.4	1 300 ppm: survival 14 000 ppm: lethal	150	710	irritation of eyes and respiratory tract
Isobutyl acetate	3.2-6.4	3 000 ppm: survival 23 000 ppm: lethal	150	700	irritation of eyes and respiratory tract
Amyl acetate	16.6	5 000 ppm: survival	100	530	narcotic
2-Ethylhexyl acetate	3.2-5.9	> 1100 ppm: survival			slightly irritating to the eyes
2-Methoxyethyl acetate	5.1-11.9	< 450 ppm:	5	24 <sup>e</sup>	
2-Ethoxyethyl acetate	4.94 <sup>b</sup>	no effect	5	27 <sup>e</sup>	slight skin irritation
Ethylene glycol mono- and diacetate	1.6-6.9				
Glyceryl triacetate	6.4-12.8	8 200 ppm: no effect			
Glyceryl tripropionate	1.6-3.2	600 ppm: no effect			
Isobutyl isobutyrate	6.4-12.8 <sup>a</sup>	650 ppm: no effect			
		5 400 ppm: lethal			

<sup>a</sup> Rabbit. <sup>b</sup> Guinea pig. <sup>c</sup> 5% (20-30 min) or 2.5% (30-60 min) are also lethal to guinea pigs. <sup>d</sup> Mouse. <sup>e</sup> Skin notation (considerable cutaneous absorption).

Other Uses. Esters can be converted into various derivatives (see Chap. 3) and are useful *intermediates* in preparative chemistry. Ethyl formate is used in the synthesis of vitamin B<sub>1</sub>. Methyl formate is converted on a large scale into formamide and formic acid; about 30 000 t/a of formic acid are produced by this route.

Natural oils, fats, and waxes are used as *lubricants* for high-speed engines. High-boiling synthetic esters that experience little change in viscosity when exposed to extremes of temperature, either high or low, have been developed for use in auto and aircraft turboengines. Examples are bis(2-ethylhexyl) sebacate [122-62-3] and glycol or polyglycol esters of branched-chain carboxylic acids. These esters are also used as hydraulic fluids.

An example of the use of esters in *pharmaceuticals* is the common analgesic aspirin [50-78-2] (2-acetoxybenzoic acid). The active salicylic acid is released only after hydrolysis in the stomach. Benzocaine [94-09-7], the ethyl ester of 4-amino-benzoic acid, is a topical anesthetic. Phenyl salicylate [118-55-8], Salol, has antipyretic, anti-rheumatic, and antiparasitic properties.

## 10. Toxicology and Occupational Health

With a few exceptions, esters have very low toxicity. Natural fats and oils are widely used in human nutrition. Table 12 lists toxicity data for commercially important esters [53], [54]–[56].

The ester group is nontoxic. However, all esters are hydrolyzed more or less rapidly on contact with water; therefore, the toxicity of their hydrolysis products must be taken into account [53].

Most esters readily penetrate skin and mucous membranes. The considerable absorption through the skin can cause health problems. Exposed skin should be thoroughly washed with soap and plenty of water; clothing should be changed.

Inhalation of highly volatile esters in high concentrations can have a narcotic effect. Secondary effects include breathlessness and fits of choking. Ester vapors should not be allowed to contact the eye. Good ventilation of the work area and wearing of breathing apparatus are generally recommended [53].

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Estrogens → Hormones

Ethane → Hydrocarbons

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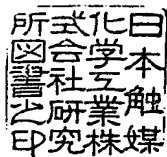


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**ERBIUM.** See LANTHANIDES.

## ESTERIFICATION

This article describes methods for the production of carboxylic esters:



For the properties of these compounds, see **ESTERS, ORGANIC**. For esters of inorganic acids, see the articles on nitric acid, phosphoric acids, sulfuric acid, etc.

Esters are most commonly prepared by the reaction of a carboxylic acid and an alcohol with the elimination of water. Esters are also formed by a number of other reactions utilizing acid anhydrides, acid chlorides, amides, nitriles, unsaturated hydrocarbons, ethers, aldehydes, ketones, alcohols, and esters (via ester interchange). Detailed reviews of esterification are given in References 1-9.

On the basis of bulk production (10), poly(ethylene terephthalate) manufacture is the most important ester producing process. This polymer is produced by either the direct esterification of terephthalic acid and ethylene glycol, or by the transesterification of dimethyl terephthalate with ethylene glycol. In 1990, poly(ethylene terephthalate) manufacture exceeded  $3.47 \times 10^6$  t/yr (see

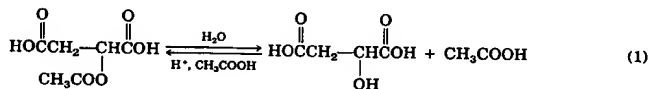
POLYESTERS). Dimethyl terephthalate is produced by the direct esterification of terephthalic acid and methanol.

Other large-volume esters are vinyl acetate [108-05-4] (VAM,  $1.15 \times 10^6$  t/yr), methyl methacrylate [80-62-6] (MMA,  $0.54 \times 10^6$  t/yr), and dioctyl phthalate [117-81-7] (DOP,  $0.14 \times 10^6$  t/yr). VAM (see VINYL POLYMERS) is produced for the most part by the vapor-phase oxidative acetoxylation of ethylene. MMA (see METHACRYLIC POLYMERS) and DOP (see PHTHALIC ACIDS) are produced by direct esterification techniques involving methacrylic acid and phthalic anhydride, respectively.

The acetates of most alcohols are also commercially available and have diverse uses. Because of their high solvent power, ethyl, isopropyl, butyl, isobutyl, amyl, and isoamyl acetates are used in cellulose nitrate and other lacquer-type coatings (see CELLULOSE, ESTERS). Butyl and hexyl acetates are excellent solvents for polyurethane coating systems (see COATINGS; URETHANE POLYMERS). Ethyl, isobutyl, amyl, and isoamyl acetates are frequently used as components in flavoring (see FLAVORS AND SPICES), and isopropyl, benzyl, octyl, geranyl, linalyl, and methyl acetates are important additives in perfumes (qv).

### Reactions Between Organic Acids and Alcohols

In the esterification of organic acids with alcohols, it has been shown that in most cases under acid catalysis, the union is between acyl and alkoxy groups. Acid hydrolysis of acetoxysuccinic acid gives malic acid with retention of configuration at the asymmetric carbon atom (11):



*n*-Amyl alcohol produced by basic hydrolysis of *n*-amyl acetate with  $^{18}\text{O}$ -enriched water does not contain  $^{18}\text{O}$  (12).

**Effect of Structure.** The rate at which different alcohols and acids are esterified as well as the extent of the equilibrium reaction are dependent on the structure of the molecule and types of functional substituents of the alcohols and acids. Specific data on rates of reaction, mechanisms, and extent of reaction are discussed in the following. More details concerning structural effects are given in References 6, 13-15.

In making acetate esters, the primary alcohols are esterified most rapidly and completely, i.e., methanol gives the highest yield and the most rapid reaction. Ethyl, *n*-propyl, and *n*-butyl alcohols react with about equal velocities and conversions. Under the same conditions, the secondary alcohols react much more slowly and afford lower conversions to ester products; however, wide variations are observed among the different members of this series. The tertiary alcohols react slowly, and the conversions are generally low (1-10% conversion at equilibrium). With isobutyl alcohol at 155°C, acids containing a straight-chain (acetic, propionic, and butyric) and phenylacetic and  $\beta$ -phenylpropionic acids are esteri-



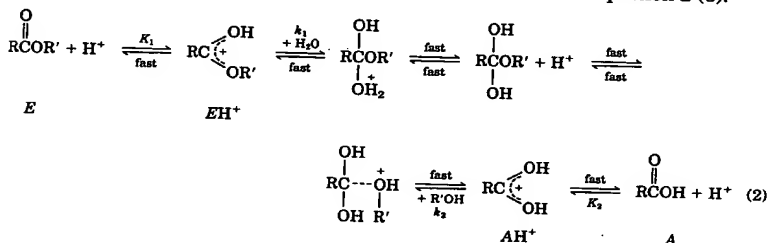
fied readily. Formic acid has the highest initial rate of reaction. The introduction of a branched chain in the acid decreases the rate of esterification, and two branches cause a still greater retarding effect. However, the conversions to ester products from these substituted acids is higher than for the normal straight-chain acids. Similarly, aromatic acids, benzoic and *p*-toluic, react slowly but have high equilibrium conversions.

The introduction of a nitrile group on an aliphatic acid has a pronounced inhibiting effect on the rate of esterification. With the chloroacetic acids, the velocity decreases with increased chlorination. Double bonds also have a retarding influence on the rate of esterification. Tests on substituted acrylic acids have shown that  $\alpha,\beta$ -unsaturated acids are esterified much less easily than the saturated analogues. A triple bond in the  $\alpha,\beta$  position has about the same effect as a double bond. A  $\beta,\gamma$ -double bond has less of a retarding action. If the double bond is sufficiently removed, as in erucic and brassidic acids (see CARBOXYLIC ACIDS), no effect is noted. Conjugated double bonds, when one is in the  $\alpha,\beta$ -position, afford a great retarding effect. Cis-substituted unsaturated acids esterify more slowly than the trans isomers.

In the preparation of ethyl esters using anhydrous ethyl alcohol and hydrogen chloride catalyst, the rate of esterification of straight-chain fatty acids from propionic through stearic is substantially constant; branching of the fatty acid chain causes retardation. In the saturated dibasic acids, the rate of esterification is a maximum at glutaric acid. The ease of esterification of the cycloparaffin monocarboxylic acids increases in the order C3, C7, C6, C5, and C4 rings; with the exception of cyclopropanecarboxylic acid, these are esterified more rapidly than the corresponding open-chain acids.

Substitutions that displace electrons toward the carboxyl group of aromatic acids diminish the rate of the reaction (16). The substitution of fluoromethoxy or ethoxy groups in the ortho position has an accelerating action, whereas iodo, bromo, nitro, or methyl groups produce retardation. The influence of groups in the meta and para positions is not nearly so marked (17).

**Kinetic Considerations.** Extensive kinetic and mechanistic studies have been made on the esterification of carboxylic acids since Berthelot and Saint-Gilles first studied the esterification of acetic acid (18). Although ester hydrolysis is catalyzed by both hydrogen and hydroxide ions (19,20), a base-catalyzed esterification is not known. A number of mechanisms for acid- and base-catalyzed esterification have been proposed (4). One possible mechanism for the bimolecular acid-catalyzed ester hydrolysis and esterification is shown in equation 2 (6).



This mechanism leads to the rate equation (eq. 3) for hydrolysis and to an analogous expression for the esterification (13):

$$-\frac{d[E]}{dt} = \frac{k_1 K_1 [E][H_2O][H^+]}{1 + \alpha} - \frac{k_2 K_2 [A][R'OH][H^+]}{1 + 1/\alpha} \quad (3)$$

In this expression,  $\alpha$  depends on those rate coefficients in the above mechanism whose values are assumed to be high. Other mechanisms for the acid hydrolysis and esterification differ mainly with respect to the number of participating water molecules and possible intermediates (21–23).

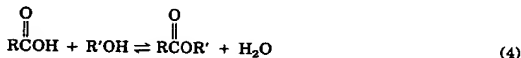
Applications of kinetic principles to industrial reactions are often useful. Initial kinetic studies of the esterification reaction are usually conducted on a small scale in a well stirred batch reactor (24). In many cases, results from batch studies can be used in the evaluation of the esterification reaction in a continuous operating configuration. Generally, the rate of esterification with acid catalyst is proportional to the acid or hydrogen ion concentration as well as the concentration of the alcohols and organic acid. The effect of temperature on the reaction rate is given by the well known Arrhenius equation. These factors are interrelated, and may be used to predict optimum operational conditions for the production of a given ester if the necessary data are available, ie, the order of the reaction under the conditions to be used, a mathematical relation describing the yield with time, and an empirical equation relating the reaction rate constant with temperature, catalyst concentration, and proportions of reactants.

With these kinetic data and a knowledge of the reactor configuration, the development of a computer simulation model of the esterification reaction is invaluable for optimizing esterification reaction operation (25–28). However, all esterification reactions do not necessarily permit straightforward mathematical treatment. In a study of the esterification of 2,3-butanediol and acetic acid using sulfuric acid catalyst, it was found that the reaction occurs through two pairs of consecutive reversible reactions of approximately equal speeds. These reactions do not conform to any simple first-, second-, or third-order equation, even in the early stages (29).

In a study of the kinetics of the reaction of 1-butanol with acetic acid at 0–120°C, an empirical equation was developed that permits estimation of the value of the rate constant with a deviation of 15.3% from the molar ratio of reactants, catalyst concentration, and temperature (30). This study was conducted using sulfuric acid as catalyst with a mole ratio of 1-butanol to acetic acid of 3:19.6, and a catalyst concentration of 0–0.14 wt %.

Similar studies have been performed on the formation of mono *n*-butyl phthalate at 80–150°C with sulfuric acid catalyst (31). The reaction of phthalic anhydride with mono *n*-butyl phthalate to afford di *n*-butyl phthalate is complete in 10 min at 100°C with 1 wt % catalyst.

**Equilibrium Constants.** The reaction between an organic acid and an alcohol to produce an ester and water is expressed in equation 4:



This was first demonstrated in 1862 by Berthelot and Saint-Gilles (32), who found that when equivalent quantities of ethyl alcohol and acetic acid were allowed to react, the esterification stopped when two-thirds of the acid had reacted. Similarly, when equal molar proportions of ethyl acetate and water were heated together, hydrolysis of the ester stopped when about one-third of the ester was hydrolyzed. By varying the molar ratios of alcohol to acid, yields of ester >66% were obtained by displacement of the equilibrium. The results of these tests were in accordance with the mass action law shown in equation 5.

$$K = \frac{[\text{ester}][\text{water}]}{[\text{acid}][\text{alcohol}]} \quad (5)$$

However, in many cases the equilibrium constant is affected by the proportion of reactants (7,33,34). The temperature as well as the presence of salts may also affect the value of the equilibrium constant (35,36).

The effect of water on the equilibrium constant for the reaction of 1 mol of ethanol, 1 mol of acetic acid, and 23 moles of water has been investigated. This mixture has an equilibrium constant of 3.56, compared with 3.79 for the reaction with anhydrous materials (7,37).

Theoretical yields of ester obtainable with proportions of reactants are shown in Figure 1 for four values of the equilibrium constant. Thus when  $K$  equals 10 (esters of *p*-toluic acid with primary alcohols), with equivalent amounts of acid and alcohol, a yield of about 76% may be expected.

In general, esters having equilibrium constants below unity are not prepared by direct interaction of alcohol and acid; in these cases, the acid anhydrides or acid chlorides are used, since the equilibrium favors the ester product.

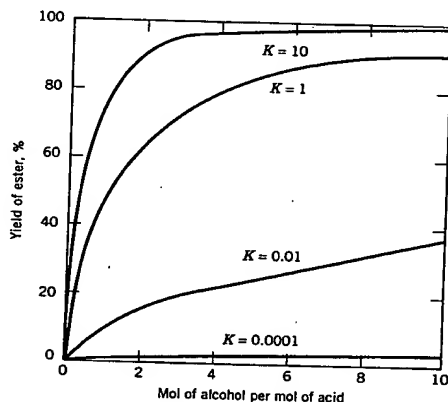


Fig. 1. Theoretical yields of ester obtainable with varying proportions of reactants for different values of equilibrium constant.

**Completion of Esterification.** Because the esterification of an alcohol and an organic acid involves a reversible equilibrium, these reactions usually do not go to completion. Conversions approaching 100% can often be achieved by removing one of the products formed, either the ester or the water, provided the esterification reaction is equilibrium limited and not rate limited. A variety of distillation methods can be applied to afford ester and water product removal from the esterification reaction (see DISTILLATION). Other methods such as reactive extraction and reverse osmosis can be used to remove the esterification products to maximize the reaction conversion (38). In general, esterifications are divided into three broad classes, depending on the volatility of the esters:

(1) Esters of high volatility, such as methyl formate, methyl acetate, and ethyl formate, have lower boiling points than those of the corresponding alcohols, and therefore can be readily removed from the reaction mixture by distillation.

(2) Esters of medium volatility are capable of removing the water formed by distillation. Examples are propyl, butyl, and amyl formates, ethyl, propyl, butyl, and amyl acetates, and the methyl and ethyl esters of propionic, butyric, and valeric acids. In some cases, ternary azeotropic mixtures of alcohol, ester, and water are formed. This group is capable of further subdivision: with ethyl acetate, all of the ester is removed as a vapor mixture with alcohol and part of the water, while the balance of the water accumulates in the system. With butyl acetate, on the other hand, all of the water formed is removed overhead with part of the ester and alcohol, and the balance of the ester accumulates as a high boiler in the system.

(3) Esters of low volatility are accessible via several types of esterification. In the case of esters of butyl and amyl alcohols, water is removed as a binary azeotropic mixture with the alcohol. To produce esters of the lower alcohols (methyl, ethyl, propyl), it may be necessary to add a hydrocarbon such as benzene or toluene to increase the amount of distilled water. With high boiling alcohols, ie, benzyl, furfuryl, and  $\beta$ -phenylethyl, an accessory azeotroping liquid is useful to eliminate the water by distillation.

**Use of Azeotropes to Remove Water.** With the aliphatic alcohols and esters of medium volatility, a variety of azeotropes is encountered on distillation (see DISTILLATION, AZEOTROPIC AND EXTRACTIVE). Removal of these azeotropes from the esterification reaction mixture drives the equilibrium in favor of the ester product (39).

Binary azeotropes may be formed between the alcohol and water, the alcohol and ester, and the ester and water. Ternary azeotropes involving the alcohol, ester, and water are also possible. In general, the ternary azeotropes have the lowest boiling points, but the differences between the boiling points of the various combinations in some instances are very small. The ester-water binaries have boiling points close to those of the ternary mixtures. An extremely efficient fractionating column is usually required to obtain a pure ternary azeotrope. Binary azeotropes of the alcohol and water may be utilized in the preparation of the higher boiling, nonvolatile esters for completion of the reaction (39). Almost all of the alcohols (up to C20-alcohols) except methanol form binary azeotropes with water. The azeotropes formed by water with ethyl, *n*-propyl, isopropyl, allyl, and *tert*-butyl alcohols are single phase, ie, on condensation of the vapor, the components are completely miscible. Other means to eliminate water are often necessary: extraction of the ester with a water-insoluble solvent, eg, benzene, cyclo-

hexane, or carbon tetrachloride; reactive distillation; drying with potassium carbonate; or salting out. The higher alcohols form azeotropes that on condensation separate into two liquid phases; in such a case, the alcohol-rich phase can be separated by further distillation into azeotrope and pure alcohol, and the water-rich phase into azeotrope and water. Under certain conditions, entraining gases are used to facilitate the removal of water (40).

*Use of Desiccants and Chemical Means to Remove Water.* Another means to remove the water of esterification is calcium carbide supported in a thimble of a continuous extractor through which the condensed vapor from the esterification mixture is percolated (41) (see CARBIDES). A column of activated bauxite (Florite) mounted over the reaction vessel has been used to remove the water of reaction from the vapor by adsorption (42).

**Catalysts.** The choice of the proper catalyst for an esterification reaction is dependent on several factors (43-46). The most common catalysts used are strong mineral acids such as sulfuric and hydrochloric acids. Lewis acids such as boron trifluoride, tin and zinc salts, aluminum halides, and organo-titanates have been used. Cation-exchange resins and zeolites are often employed also.

In laboratory preparations, sulfuric acid and hydrochloric acid have classically been used as esterification catalysts. However, formation of alkyl chlorides or dehydration, isomerization, or polymerization side reactions may result. Sulfonic acids, such as benzenesulfonic acid, *p*-toluenesulfonic acid, or methanesulfonic acid, are widely used in plant operations because of their less corrosive nature. Phosphoric acid is sometimes employed, but it leads to rather slow reactions. Soluble or supported metal salts minimize side reactions but usually require higher temperatures than strong acids.

*Acid-Regenerated Cation Exchangers.* The use of acid-regenerated cation resin exchangers (see ION EXCHANGE) as catalysts for effecting esterification offers distinct advantages over conventional methods. Several types of cation-exchange resins can be used as solid catalysts for esterification (47,48). In general, the strongly acidic sulfonated resins comprised of copolymers of styrene, ethylvinylbenzene, and divinylbenzene are used most widely. With the continued improvement of ion-exchange resins, such as the macroporous sulfonated resins, esterification has become one of the most fertile areas for use of these solid catalysts. With low molecular weight acids and alcohols, in most cases the resin structure has minimal effect on the yield or kinetics of the esterification as long as the catalyst contains strongly acidic groups. The kinetics in batch and tubular reactors of the esterification of 1-butanol with acetic acid catalyzed by a macroporous sulfonated polystyrene exchange resin have been studied. The catalytic activity was dependent on the water content of the resin and the rate determining step is the surface reaction of the chemisorbed acid and adsorbed alcohol (49).

Despite the higher cost compared with ordinary catalysts, such as sulfuric or hydrochloric acid, the cation exchangers present several features that make their use economical. The ability to use these agents in a fixed-bed reactor operation makes them attractive for a continuous process (50,51). Cation-exchange catalysts can be used also in continuous stirred tank reactor (CSTR) operation.

The resin (Amberlite IR-116 and Amberlite IR-120B) catalyzed continuous esterification of butanol or 2-ethylhexanol with acrylic acid is a novel example. High conversion and selectivity to the acrylate ester are accomplished. The CSTR in this application has advantage over a fixed-bed configuration since water sep-

aration from the higher boiling ester product in the reactor is more rapid, and this leads to a higher conversion with fewer by-products. The type of exchange resin also affects the esterification. The degree of cross-linking, porosity, and surface area of the strongly acid cation-exchange resin in combination with the back-mixed reactor design are critical factors to minimize secondary by-product formation and polymeric fouling of the resin catalyst (46).

The esterification of *n*-butyl alcohol and oleic acid with a phenol-formaldehyde-sulfonic acid resin (similar to amberlite IR-100) is essentially second order after an initial slow period (52). The velocity constant is directly proportional to the surface area of the catalyst per unit weight of reactants.

A series of tests using Amberlite IR-12 (sulfonated polystyrene resin) to esterify diethylene glycol (DEG) using toluene as the entrainer for removal of water gave the results in Table 1 (53).

Recovery of dilute acetic acid is achieved by esterification with methanol using a sulfonated resin (Dowex 50w) in a packed distillation column (54). Pure methyl acetate is obtained. This reaction is second order in acetic acid, zero order in methanol, and partially diffusion controlled.

**Table 1. Tests Using Amberlite IR-120 to Esterify Diethylene Glycol (DEG)**

Acid	DEG, mol/mol acid	IR-120, g/100 g acid	Temp, °C	Reaction time, h	Monoester, % conv	Diester, % conv
lauric	1	7.5	140	18	24	71
lauric	4	15.5	130	10	71	21
lauric	6	7.5	140	18	86	11
lauric	12	15.0	132	18	100	
oleic	12	10.6	140	18	100	
stearic	12	8.9	150	18	100	
benzoic	2	24.6	140	4	75	

### Batch Esterification

**Ethyl Acetate.** A typical plant configuration for production of ethyl acetate [141-78-6] as a low boiling overhead product relative to water is shown in Figure 2 (2). The esterification reactor is a cylindrical tank, or still pot, heated by a closed-coil steam pipe. The reactor is charged with acetic acid, 95% ethanol, and concentrated sulfuric acid. The temperature at the top of the fractionating column is maintained at ca 70°C to give a ternary azeotropic mixture of ca 83% ethyl acetate, 9% alcohol, and 8% water. The vapor is condensed, part of it is returned to the top plate of the column as reflux, and the remainder is drawn off to storage. The ternary azeotrope (production-grade ethyl acetate) is satisfactory for many commercial purposes, but for an alcohol-free and water-free ester, further purification is needed.

***n*-Butyl Acetate.** Equipment used for the batch esterification to give butyl acetate [123-86-4] is shown in Figure 3. Glacial acetic acid is mixed with an excess of butyl alcohol and a small amount of concentrated sulfuric acid in the esterification reactor. The mixture is heated for several hours by means of a steam jacket

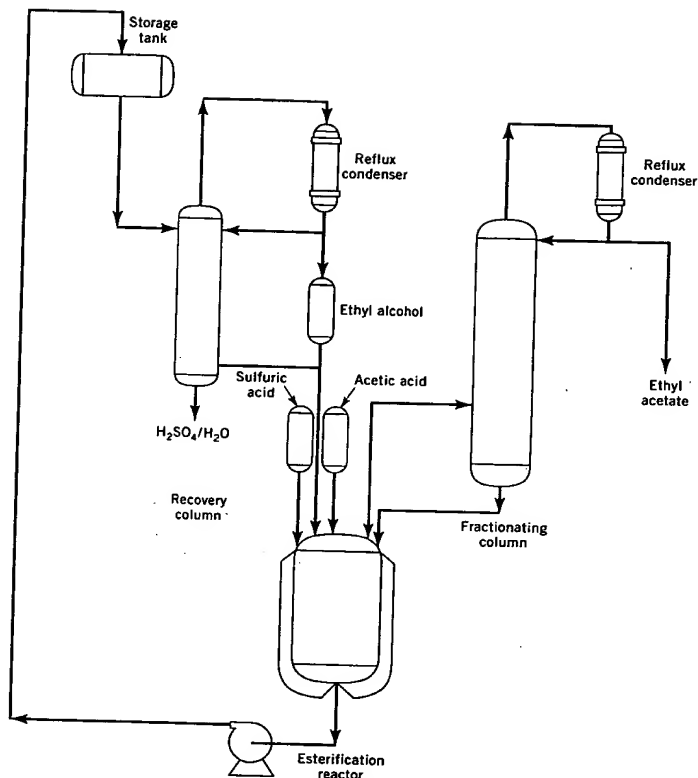


Fig. 2. Batch ethyl acetate process (2).

to give esterification equilibrium. After the preliminary heating, slow rectification is permitted to remove the water already formed and thus increase the yield. The esterification is continued until no more water separates. At this point, the temperature at the top of the column rises, and the percentage of acetic acid in the distillate increases. It is necessary to neutralize the small amount of acid remaining in the esterification reactor before further distillation. A solution of sodium hydroxide is added to the esterification reactor, and the mixture is allowed to stand to form a water layer that is removed. The organic ester layer (upper layer) is then washed with water and distilled to obtain an overhead butyl acetate product of 75–85% purity; the remainder is butyl alcohol.

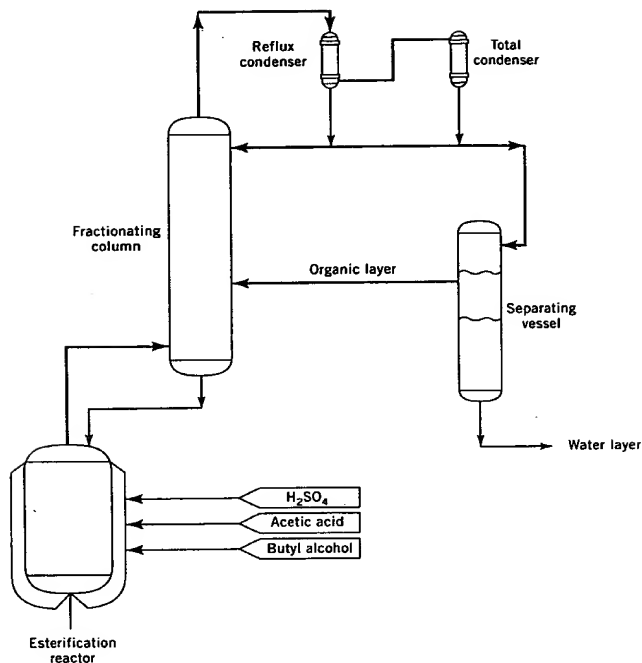


Fig. 3. Batch *n*-butyl acetate process (2).

### Continuous Esterification

The law of mass action, the laws of kinetics, and the laws of distillation all operate simultaneously in a process of this type. Esterification can occur only when the concentrations of the acid and alcohol are in excess of equilibrium values; otherwise, hydrolysis must occur. The equations governing the rate of the reaction and the variation of the rate constant (as a function of such variables as temperature, catalyst strength, and proportion of reactants) describe the kinetics of the liquid-phase reaction. The usual distillation laws must be modified, since most esterifications are somewhat exothermic and reaction is occurring on each plate. Since these kinetic considerations are superimposed on distillation operations, each plate must be treated separately by successive calculations after the extent of conversion has been determined (see DISTILLATION).

Continuous esterification of acetic acid in an excess of *n*-butyl alcohol with sulfuric acid catalyst using a four-plate single bubblecap column with reboiler has



been studied (55). The rate constant and the theoretical extent of reaction were calculated for each plate, based on plate composition and on the total incoming material to the plate. Good agreement with the analytical data was obtained.

A continuous distillation process has been studied for the production of high boiling esters from intermediate boiling polyhydric alcohols and low boiling monocarboxylic aliphatic or aromatic acids (56). The water of reaction and some of the organic acid were continuously removed from the base of the column.

**Methyl Acetate.** High purity methyl acetate [79-20-9] is required for the rhodium catalyzed carbonylation process to produce acetic anhydride (57). In the most recently developed commercial process for the manufacture of high purity methyl acetate, acetic acid functions both as a reactant and as an extractant in a countercurrent reactive distillation column (58,59), thereby alleviating the problem of azeotrope formation. This methyl acetate purification process obviates the use of additional vacuum or extractive distillation means to separate methyl acetate from its low boiling water and methanol azeotropes (60,61). As shown in Figure 4, this process uniquely demonstrates the use of reactive distillation as a means to produce essentially dry methyl acetate. The esterification reaction cat-

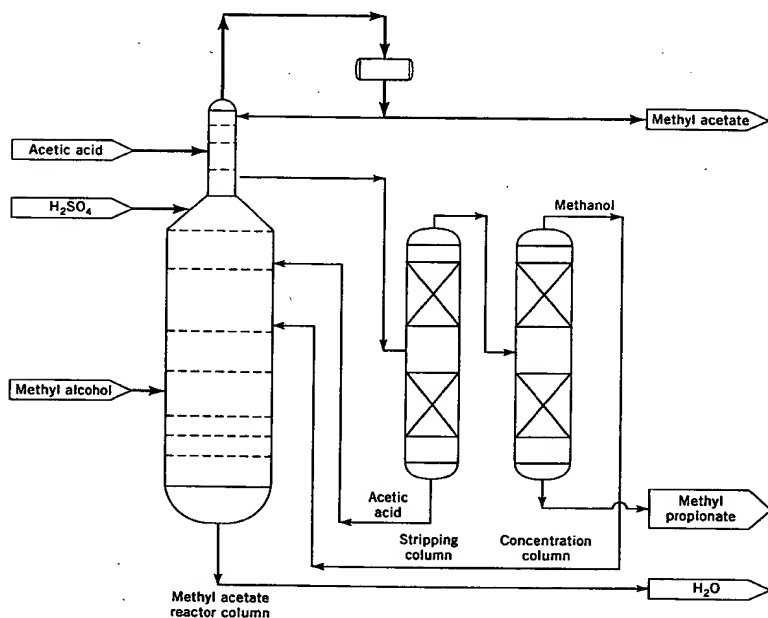


Fig. 4. Continuous methyl acetate process (59).

alyzed by sulfuric acid occurs in the middle of the column. Acetic acid is fed to the top portion of the reactor section, and the methanol is fed to the lower portion of the reactor section. The countercurrent flow of acetic acid and methyl acetate with its azeotropes is used to remove water and by-products from methyl acetate. Below the acetic acid feed and above the reaction section, water and some methanol are extracted from methyl acetate using acetic acid. Acetic acid and methyl acetate are then separated above the acetic acid feed in the rectification portion of the column. High purity methyl acetate (at least 99.5 wt % methyl acetate) is isolated from the column overhead. The catalyst and impurities (primarily methyl propionate and isopropyl acetate) are removed from the reactor section by a sidedraw. Methanol in turn is stripped from the water in the lower portion of the column below the methanol feed. The impurities are further concentrated and removed from the process in two distillation columns with catalyst and acetic acid being recycled back to the reactive distillation column.

**Ethyl Acetate.** The production of ethyl acetate by continuous esterification is an excellent example of the use of azeotropic principles to obtain a high yield of ester (2). The acetic acid, concentrated sulfuric acid, and an excess of 95% ethyl alcohol are mixed in reaction tanks provided with agitators. After esterification equilibrium is reached in the mixture, it is pumped into a receiving tank and through a preheater into the upper section of a bubblecap plate column (Fig. 5). The temperature at the top of this column is maintained at ca 80°C and its vapor (alcohol with the ester formed and ca 10% water) is passed to a condenser. The first recovery column is operated with a top temperature of 70°C, producing a ternary azeotrope of 83% ester, 9% alcohol, and 8% water. The ternary mixture is fed to a static mixer where water is added in order to form two layers and allowed to separate in a decanter. The upper layer contains ca 93% ethyl acetate, 5% water, and 2% alcohol, and is sent to a second recovery or ester-drying column. The overhead from this column is 95–100% ethyl acetate which is sent to a cooler and then to a storage tank. This process also applies to methyl butyrate.

### Vapor-Phase Esterification

Catalytic esterification of alcohols and acids in the vapor phase has received attention because the conversions obtained are generally higher than in the corresponding liquid-phase reactions (7).

**Physicochemical Considerations.** The determination of the equilibrium constant  $K_G$  for the reaction  $C_2H_5OH + CH_3COOH = C_2H_5OOCCH_3 + H_2O$  has been the subject of a number of investigations over the temperature range of 40–300°C (62). The values of the equilibrium constant range from 6–559 (63) with 71–95% ester as the equilibrium concentration from an equimolar mixture of ethyl alcohol and acetic acid, depending on the technique used. A study of the reaction mechanism indicates that adsorption of acetic acid is the rate-controlling step; the molecularly adsorbed acetic acid then reacts with alcohol in the vapor phase. The rate of esterification of acetic acid and ethyl alcohol in equimolar quantities has been studied in a dynamic system using silica gel catalyst at 150–270°C (64).

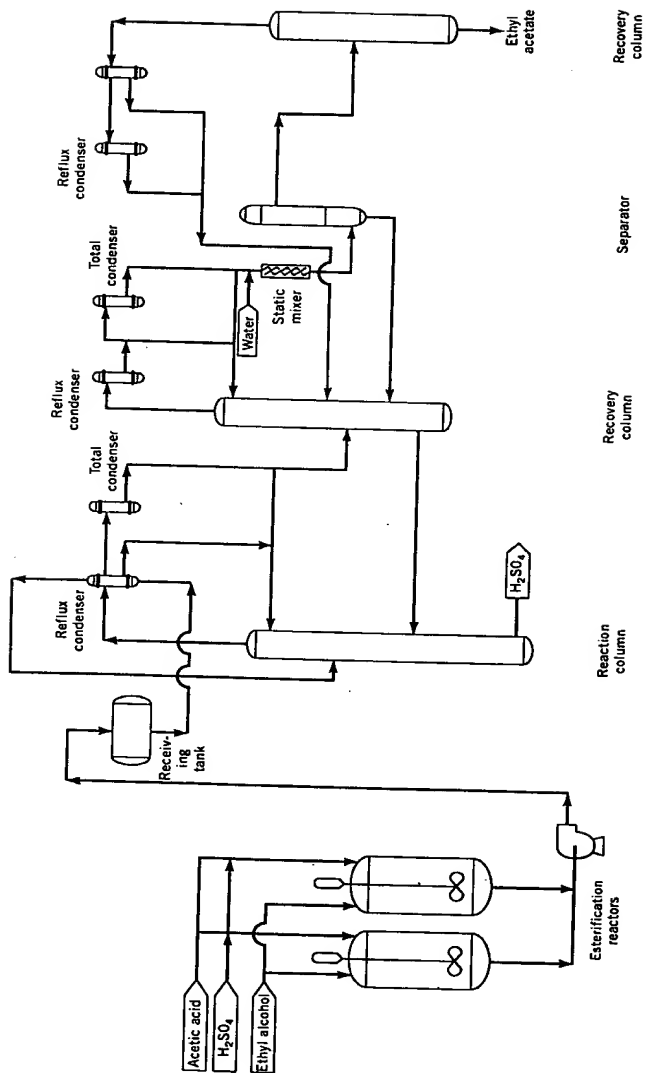


Fig. 5. Continuous ethyl acetate process (2).

**Ethyl Acetate.** Catalysts proposed for the vapor-phase production of ethyl acetate include silica gel, zirconium dioxide, activated charcoal, and potassium hydrogen sulfate. More recently, phosphoric-acid-treated coal (65) and calcium phosphate (66) catalysts have been described.

**Other Esters.** The esterification of acetic acid with various alcohols in the vapor phase has been studied using several catalysts precipitated on pumice (67).

### Esterification of Other Compounds

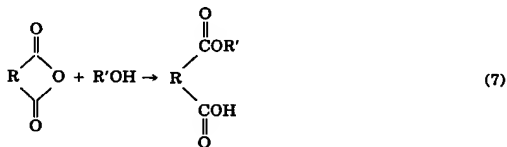
**Acid Anhydrides.** Acid anhydrides react with alcohols to form esters (in high yields in many cases) with a carboxylic acid formed as by-product:



However, this method is applied only when esterification cannot be effected by the usual acid-alcohol reaction because of the higher cost of the anhydrides. The production of cellulose acetate (see FIBERS, CELLULOSE ESTERS), phenyl acetate (used in acetaminophen production), and aspirin (acetylsalicylic acid) (see SALICYLIC ACID) are examples of the large-scale use of acetic anhydride. The speed of acylation is greatly increased by the use of catalysts (68) such as sulfuric acid, perchloric acid, trifluoroacetic acid, phosphorus pentoxide, zinc chloride, ferric chloride, sodium acetate, and tertiary amines, eg, 4-dimethylaminopyridine.

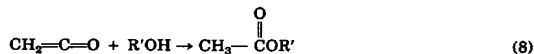
Formic anhydride is not stable. However, formate esters of alcohols and phenolics can be prepared using formic-acetic anhydride (69,70). Anhydrides can also be incorporated into polystyrene backbones which can then be treated with alcohols to afford the corresponding esters and carboxypolystyrene for recycle (71).

Dibasic acid anhydrides such as phthalic anhydride and maleic anhydride readily react with alcohols to form the monoalkyl ester:



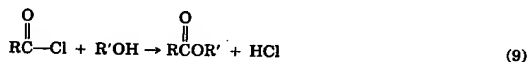
This reaction can be used for identification of individual alcohols because of the wide variations noted in the melting points of monoalkyl esters up to the dodecyl derivatives. The reaction can be used to separate alcohols of various classes. Monoesters are converted into the normal diesters by heating with an excess of alcohol and a catalyst; however, diesters are generally formed directly from the corresponding diacids.

Ketene, like acid anhydrides, reacts with alcohols to form (acetate) esters:

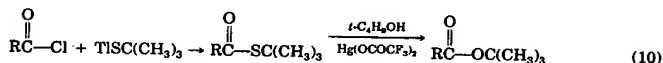


Ketene is an efficient acetylating agent with some alcohols, but in the absence of catalysts may be either nonreactive or sluggish with others, especially phenols and tertiary alcohols (72) (see KETENES AND RELATED SUBSTANCES).

**Acid Chlorides.** Acid chlorides react with alcohols to form esters:



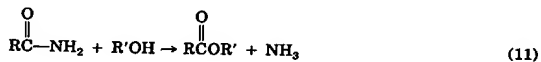
The acid chlorides are generally more reactive than the corresponding acid anhydrides. In fact, the alcoholysis of acid chlorides is probably the best laboratory method for preparing esters. Frequently, basic materials are added during the course of the reaction to neutralize by-product hydrochloric acid. When the basic material is aqueous caustic, the procedure is referred to as the Schotten-Baumann procedure (73). Esterification of tertiary alcohols by acid chlorides is described in Reference 74. Esters of tertiary alcohols can also be formed through an intermediate *t*-butyl thioate group (75):



Acid chlorides are used for the quantitative determination of hydroxyl groups and for acylation of sugars. Industrial applications include the formation of the alkyl or aryl carbonates from phosgene (see CARBONIC AND CHLOROFORMIC ESTERS) and phosphate esters such as triethyl, triphenyl, tricresyl, and tritolyl phosphates from phosphorus oxychloride (see PHOSPHORIC ACIDS).

The reaction of alcohols and acid chlorides in the presence of magnesium has been described (68). With primary and secondary alcohols the reaction is very smooth, and affords high and sometimes quantitative yields. Difficultly esterifiable hydroxy compounds such as tertiary alcohols and phenols can be esterified by this method. The reaction carried out in ether or benzene is usually very vigorous with evolution of hydrogen.

**Amides.** Alcoholysis of amides provides another method for synthesizing esters:



In order to produce high yields of ester in this manner it is necessary to remove the by-product ammonia (or amine) either by heating or combining with mineral acid, eg,  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ . Recent work has shown that acidic ion-exchange resins can be used in place of mineral acids for converting sensitive unsubstituted amides (76). The structural relationships involved in esterification of amides are shown in Table 2 (77).

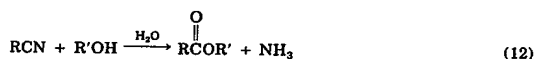
Other methods of converting amides to esters have been described (78). Alkyl halides can be treated with amides to give esters (79). Also, esters can be synthe-

Table 2. Comparative Yields of Esters from Amides or Acids

Methyl ester	Yield of ester, %	
	From amide	From acid
formate	34	
acetate	70	56
monochloroacetate	64	65
dichloroacetate	57	70
trichloroacetate	53	73
phenylacetate	50	86
propionate	80	44
benzoate	15	37

sized from *N*-alkyl-*N*-nitrosoamides, which are derived from the corresponding amides (80).

**Nitriles.** Alcoholysis of nitriles offers a convenient way to produce esters without isolating the acid:



Acids are used to combine with the ammonia formed. A large excess of alcohol is used, but the amount of water is generally kept small. Catalysts such as hydrogen chloride, hydrogen bromide, and sulfuric acid have been employed (71).

One of the most important applications of this process is that of methyl methacrylate manufacture. In this process (81), acetone cyanohydrin is treated with sulfuric acid at 100°C, affording the corresponding methacrylamide sulfate which is esterified with methanol. After purification, methyl methacrylate (99.8% purity) is obtained in a yield of ca 85%.

**Unsaturated Hydrocarbons.** Olefins from ethylene through octene have been converted into esters via acid-catalyzed nucleophilic addition. With ethylene and propylene, only a single ester is produced using acetic acid, ethyl acetate and isopropyl acetate, respectively. With the butylenes, two products are possible: *sec*-butyl esters result from 1- and 2-butylenes, whereas *tert*-butyl esters are obtained from isobutylene. The C5 olefins give rise to three *sec*-amyl esters and one *t*-amyl ester. As the carbon chain is lengthened, the reactivity of the olefin with organic acids increases.

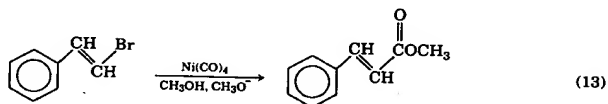
In the case of ethylene, it is necessary to use high temperatures and pressures as well as active catalyst to effect esterification (82). Yields of 40–50% based on ethylene were obtained with boron trifluoride–hydrogen fluoride mixtures as catalysts at 150°C. 2-Butene under pressure at 115–120°C with an excess of glacial acetic acid containing 10% H<sub>2</sub>SO<sub>4</sub> gave as much as a 60% yield of *sec*-butyl acetate (83).

*tert*-Butyl acetate [540-88-5] was prepared by passing isobutylene and acetic acid (2:1 mol ratio) in the liquid phase over a silica catalyst impregnated with

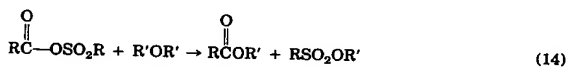
vanadium pentoxide and potassium sulfate at 1.7 MPa (250 psi). Conversion of isobutylene to ester increased with increasing temperature and ranged from 10% at 52°C to 24% at 93°C. Based on the acetic acid charged, yields of 31–43% of *t*-butyl acetate resulted at 93°C (84).

Most of the vinyl acetate produced in the United States is made by the vapor-phase ethylene process. In this process, a vapor-phase mixture of ethylene, acetic acid, and oxygen is passed at elevated temperature and pressures over a fixed-bed catalyst consisting of supported palladium (85). Less than 70% oxygen, acetic acid, and ethylene conversion is realized per pass. Therefore, these components have to be recovered and returned to the reaction zone. The vinyl acetate yield using this process is typically in the 91–95% range (86). Vinyl acetate can be manufactured also from acetylene, acetaldehyde, and the liquid-phase ethylene process (see VINYL POLYMERS).

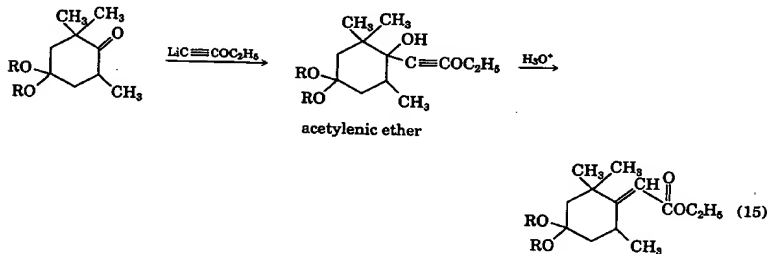
Esters can be obtained from halogenated olefins using a metal carbonyl catalyst (87), eg, *trans*-1-bromo-2-phenylethylene is treated with nickel carbonyl in the presence of methanol to afford the corresponding methyl cinnamate (see CINNAMIC ACID).



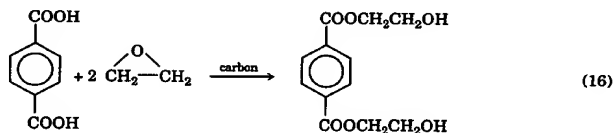
**Ethers.** In the presence of anhydrous agents such as ferric chloride (88), hydrogen bromide, and acid chlorides, ethers react to form esters (see ETHERS). Esters can also be prepared from ethers by an oxidative process (89). With mixed sulfonic-carboxylic anhydrides, ethers are converted to a mixture of the corresponding carboxylate and sulfonate esters (90):



Unsaturated esters can be prepared from the corresponding acetylenic ethers with yields in most cases of >50% (91) as in the following example:



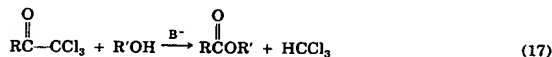
$\beta$ -hydroxyethyl esters can be prepared from carboxylic acids and ethylene oxide:



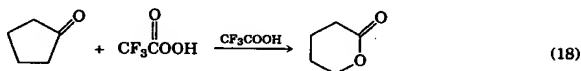
Bis-( $\beta$ -hydroxyethyl) terephthalate and related compounds can be produced in this manner using finely divided carbon catalyst (92). The carbon functions not only as a catalyst but also helps to remove color from the reaction mixture upon removal of the carbon by hot filtration.

**Aldehydes and Ketones.** Esters are obtained readily by condensation of aldehydes in the presence of alcoholate catalysts such as aluminum ethylate,  $\text{Al}(\text{OC}_2\text{H}_5)_3$ , by the Tishchenko reaction. The alcoholate catalysts may be prepared from commercial aluminum and *n*-butyl or isobutyl alcohol in the presence of 2–5% aluminum chloride (93).

Trihalomethyl ketones react with alcohols in the presence of alkaline catalysts even at room temperature (94):

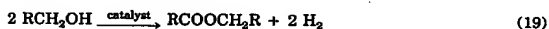


A variety of esters can be prepared from the corresponding ketones using peracids in a process usually referred to as the Baeyer-Villiger reaction (95); ie, cyclopentanone is converted to  $\delta$ -valerolactone upon treatment of the ketone with peroxytrifluoroacetic acid:



This conversion can be carried out, in many cases, with >80% yield.

**Alcohols.** The direct synthesis of esters by dehydrogenation or oxidative hydrogenation of alcohols offers a simple method for the preparation of certain types of esters, such as ethyl acetate (96–98):



The reaction is catalyzed by copper with various promoters or activators, and is carried out in the vapor phase at 200–300°C.

### Technical Preparation of Esters

Esterification is generally carried out by refluxing the reaction mixture until the carboxylic acid has reacted with the alcohol and the water has been split off. The



water or the ester is removed from the equilibrium by distillation. The choice of the esterification process to obtain a maximum yield is dependent on many factors, ie, no single process has universal applicability. Although extensive preparative techniques have been reviewed elsewhere (7,68), the methods given in this section are representative of both laboratory and plant-scale techniques used in batch esterifications.

**Methyl Esters.** Methyl esters are obtained in good yield using methylene dichloride or ethylene dichloride as solvent (99). The latter is generally preferred, but the choice of the solvent depends to some extent on the boiling point of the desired ester. Also, the toxicity of these solvents should be considered prior to using them (see CHLOROCARBONS AND CHLOROHYDROCARBONS). The general procedure is as follows: for each mole of aliphatic carboxyl group, 96 g (3 mol) of methanol, 300 mL of ethylene dichloride, and 3 mL of concentrated  $H_2SO_4$  are used. With aromatic acids, the amount of  $H_2SO_4$  is increased to 15 mL/mol of carboxyl group. The mixture is refluxed for 6–15 h, although in some cases the time may be as short as 30 minutes. Progress of esterification is usually indicated by the development of cloudiness and separation of an upper layer containing water, methanol, and sulfuric acid. After the reaction is completed, the cooled mixture is washed successively with water, sodium bicarbonate solution, and again with water. The ethylene chloride layer is then distilled at atmospheric or reduced pressure, and the residual methyl ester is purified by distillation or crystallization.

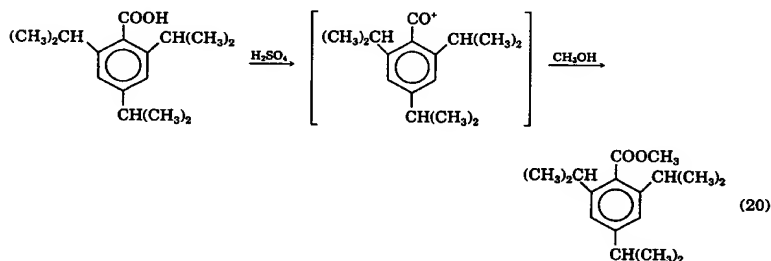
The manufacture of high purity methyl acetate by a reactive distillation process has been accomplished; high conversion of one reactant can be achieved only with a large excess of the other reactant. Because the reaction is reversible, the rate of reaction in the liquid phase is increased by removing methyl acetate preferentially to the other components in the reaction mixture (100).

**Medium Boiling Esters.** Esterification of ethyl and propyl alcohols, ethylene glycol, and glycerol with various acids, eg, chloro- or bromoacetic, or pyruvic, by the use of a third component such as benzene, toluene, hexane, cyclohexane, or carbon tetrachloride to remove the water produced is quite common. Benzene has been used as a co-solvent in the preparation of methyl pyruvate from pyruvic acid (101). The preparation of ethyl lactate is described as an example of the general procedure (102). A mixture of 1 mol 80% lactic acid and 2.3 mol 95% ethyl alcohol is added to a volume of benzene equal to half that of the alcohol (ca 43 mL), and the resulting mixture is refluxed for several hours. When distilled, the overhead condensate separates into layers. The lower layer is extracted to recover the benzene and alcohol, and the water is discarded. The upper layer is returned to the column for reflux. After all the water is removed from the reaction mixture, the excess of alcohol and benzene is removed by distillation, and the ester is fractionated to isolate the pure ester.

**High Boiling Esters.** The following procedure can be used for making diethyl phthalate and other high boiling esters (103). Phthalic anhydride (1 equiv) and 2.5 equivalents of ethanol are refluxed for 2 h in the presence of 1% of concentrated  $H_2SO_4$ . To produce the monoester, the excess of alcohol is distilled at  $<100^\circ C$ . For the diester, a mixture of 67% benzene and 33% alcohol is introduced continuously below the surface of the reaction mixture and the resulting alcohol–water–benzene ternary is distilled and condensed. A yield of diester of  $>99\%$  is

obtained by passing 3.4–7 equivalents of alcohol through the mixture in 4.5–7 hours. In another continuous process for the production of diesters, the mixture of alcohol, acid, and the catalyst is introduced into the upper part of a distillation column and an excess of the alcohol is introduced into the bottom. The column is heated so that the ester, water, and excess alcohol are distilled off (104). Organotitanates, zirconates, or organotin compounds are effective catalysts for the esterification of carboxylic acids or anhydrides with higher boiling monohydroxy alcohols at temperatures that permit the continuous distillation of the water formed (105). Refluxing 1 mol phthalic anhydride with 3 mol 2-ethyl-2-hexanol with stirring using these agents, then removing the water by a trap separator gives the corresponding esters in ~99% yields (see PHTHALIC ACID). Phthalic anhydride has been esterified with >99% conversion with 10–30% excess alcohol in the presence of 0.8–1.5 mol % alkyl titanate containing 0.08–0.2% activating agent in a vertical, multistage reactor connected to a devolatilization column and filter (106).

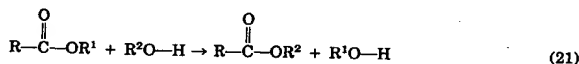
**Difficultly Esterifiable Acids.** The sterically hindered acids, such as 2,6-disubstituted benzoic acids, cannot usually be esterified by conventional means. Several esters of sterically hindered acids such as 2,4,6-triisopropylbenzoic acid [49623-71-4] have been prepared by dissolving 2 g of the acid in 14–20 mL of 100%  $\text{H}_2\text{SO}_4$  (107). After standing a few minutes at room temperature, when presumably the acylium cation is formed (eq. 20), the solution is poured into an excess of cold absolute methanol. Most of the alcohol is removed under reduced pressure, about 50 mL of water is added, and the distillation is continued under reduced pressure to remove the remainder of the methanol. The organic matter is extracted with ether and treated with sodium carbonate solution. The ester is then distilled. Yields of esters made in this manner are 57–81%.



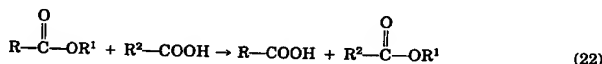
### Ester Interchange

Ester interchange (transesterification) is a reaction between an ester and another compound, characterized by an exchange of alkoxy groups or of acyl groups, and resulting in the formation of a different ester. The process of transesterification is accelerated in the presence of a small amount of an acid or a base.

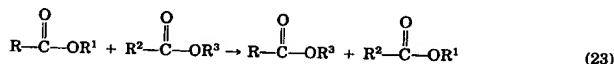
Three types of transesterification are known: (1) exchange of alcohol groups, commonly known as alcoholysis. In this process the compound with which an ester reacts is an alcohol:



(2) exchange of acid groups, acidolysis. In this process the compound with which an ester reacts is an acid:



(3) ester-ester interchange. In this process an exchange takes place between two esters:



These reactions are reversible and ordinarily do not involve large energy changes.

#### ESTER-ALCOHOL INTERCHANGE

**Reaction Conditions.** Alcoholysis commonly takes place in one liquid phase, sometimes with one of the reactants being only partially soluble and going into solution gradually as the reaction proceeds. Unless an excess of one of the reactants is used, or unless one of the products is withdrawn from the reaction phase by vaporization or precipitation, the reaction does not proceed to completion but comes to a standstill with substantial proportions of both alcohols and both esters in equilibrium. The concentrations present at equilibrium depend on the characteristics of the alcohols and esters involved, but in most practical uses of the reaction, one or both of the devices mentioned are used to force the reaction toward completion.

**Temperatures.** With alkaline catalysts, the reaction often takes place at RT or even lower temperatures. With acid catalysts, temperatures near 100°C are commonly used. With no catalyst, temperatures ~250°C may be required for a practical reaction rate.

**Catalysts.** Of the alkaline catalysts, alkali metal alkoxides are the most effective; ordinarily, the sodium or potassium alkoxide of the alcohol entering the reaction is preferred. Various other catalysts of milder alkalinity are preferred in special cases. For example, the use of sodium methyl carbonate as catalyst in the methanolysis of poly(vinyl acetate) is said to yield a poly(vinyl alcohol) having improved color. Aluminum alkoxide has been proposed as a catalyst for the alcoholysis of certain unsaturated esters; other sensitive esters have been made with a Grignard reagent as catalyst. Zinc is reported to be an efficient catalyst in the alcoholysis of ethyl esters of  $\alpha$ -halogenated aliphatic acids by allyl and methallyl alcohols; conventional catalysts favor undesirable side reactions. Neutral

organic titanates have received much attention (108). Divalent metal salts such as zinc or manganese acetate and organotin compounds such as dibutyltin oxide have been employed.

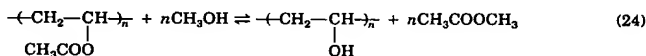
Among the acid catalysts, sulfuric acid, sulfonic acids, and hydrochloric acid are most used. With polyhydric alcohols, sulfuric acid is preferred to hydrochloric acid because of the tendency of hydrochloric acid to form chlorohydrins.

**Equilibrium.** In general, primary alcohols are more reactive than secondary alcohols (that is, they tend to displace them), and secondary alcohols tend to displace tertiary alcohols, but in addition, there are considerable differences among different members of the same class. Various alcohols have been compared in this way (4,109).

**Applications.** Transesterifications via alcoholysis play a significant role in industry as well as in laboratory and in analytical chemistry. The reaction can be used to reduce the boiling point of esters by exchanging a long-chain alcohol group with a short one, eg, methanol, in the analysis of fats, oils, and waxes. For more details see References 7 and 68. A few examples are given below.

*n*-Butyl Oleate. Olive oil, 3 kg, consisting mainly of the glyceryl esters of oleic acid, is refluxed for 20 h with 7 L of *n*-butyl alcohol containing 150 g of concentrated  $H_2SO_4$ . The product contains a small proportion of saturated esters (110).

*Poly(vinyl alcohol).* Poly(vinyl alcohol) (see VINYL POLYMERS) is more easily prepared, in a form that can be filtered and washed in a practical way, by alcoholysis of poly(vinyl acetate), than by its saponification in an aqueous system:



The use of a catalytic quantity of alkali equivalent to only a small fraction of the acetate has the advantage that contamination of the poly(vinyl alcohol) with salts, which are difficult to remove, is minimized. A variant of the process is the use of a mixture of alcohol with the acetate ester produced by the alcoholysis as the alcoholyzing agent. This provides a means of controlling the completeness of removal of the acetate groups from the poly(vinyl acetate) (111).

**Acrylic Esters.** A procedure has been described for preparation of higher esters from methyl acrylate that illustrates the use of an acid catalyst together with the removal of one of the products by azeotropic distillation (112). Another procedure for the preparation of butyl acrylate, secondary alkyl acrylates, and hydroxyalkyl acrylates using *p*-toluenesulfonic acid as a catalyst has been described (113). Aluminum isopropoxide catalyzes the reaction of amino alcohols with methyl acrylate and methyl methacrylate. A review of the synthesis of acrylic esters by transesterification is given in Reference 114 (see ACRYLIC ACID AND DERIVATIVES).

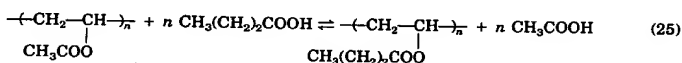
#### ESTER-ACID INTERCHANGE

Acidolysis requires the use of an elevated temperature, the use of an acid catalyst (7), or both. Like alcoholysis, the reaction is reversible and requires the use of an excess of the replacing acid or removal of one of the products from the reaction if a high degree of replacement of the acid radical of an ester by another acid is to

be obtained. This can be accomplished by distilling one of the products from the reaction mixture during the acidolysis.

In a series of organic acids of similar type, not much tendency exists for one acid to be more reactive than another. For example, in the replacement of stearic acid in methyl stearate by acetic acid, the equilibrium constant is 1.0. However, acidolysis in formic acid is usually much faster than in acetic acid, due to higher acidity and better ionizing properties of the former (115). Branched-chain acids, and some aromatic acids, especially sterically hindered acids such as ortho-substituted benzoic acids, would be expected to be less active in replacing other acids. Mixtures of esters are obtained when acidolysis is carried out without forcing the replacement to completion by removing one of the products. The acidolysis equilibrium and mechanism are discussed in detail in Reference 115.

An industrial example of acidolysis is the reaction of poly(vinyl acetate) with butyric acid to form poly(vinyl butyrate). Often a butyric acid-methanol mixture is used and methyl acetate is obtained as a coproduct.



#### ESTER-ESTER INTERCHANGE

The reaction between two esters to produce two other esters was described by Friedel and Crafts in 1865, but has not been used as much as alcoholysis. The same general principles apply with regard to reversibility of the reaction and the means of driving the reaction to completion (7). In general, the same catalysts are effective as in alcoholysis. Usually the reaction is slower than alcoholysis of the same esters. Without a catalyst, a reaction time of several h at  $>250^\circ\text{C}$  is required to bring two typical esters to equilibrium. Catalysts are almost essential to bring reaction rates into a practical range so that the use of destructive temperatures can be avoided. Tin compounds, especially stannous hydroxide, have been mentioned frequently as catalysts and do not produce much decomposition or discoloration of the esters (116). More effective at lower temperatures are the acid catalysts, such as sulfuric acid and sulfonic acids, and especially the alkaline catalysts such as sodium alkoxides. With an alkaline catalyst, ester-ester interchange can be carried out at temperatures as low as  $0^\circ\text{C}$ .

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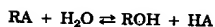
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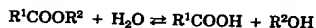


## ESTERS, ORGANIC

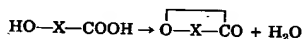
Esters are compounds that, on hydrolysis, yield alcohols or phenols and acids according to the equation:



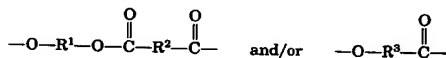
where R is a hydrocarbon fragment and A is the anion portion of an organic acid. For carboxylic acid esters, the reaction can be represented as:



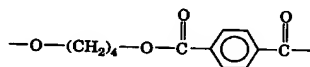
where  $R^1$  and  $R^2$  are the same or different hydrocarbon radicals. The reverse reaction constitutes the usual method for preparing esters (see ESTERIFICATION). When  $R^1$  and  $R^2$  are bonded together, the resultant cyclic ester is called a lactone. Lactones can be produced from molecules containing both carboxyl and hydroxy groups.



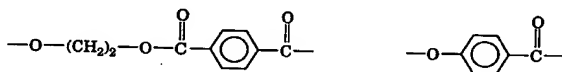
Polyesters are polymers with basic structural units:



where  $R^1$ ,  $R^2$ , and  $R^3$  are alkyl, aromatic, or alkyl-aromatic radicals and they may be the same or different. For example, poly(butylene terephthalate) [26062-94-2] has the repeating unit



whereas poly(ethylene terephthalate-*p*-oxybenzoate) [25822-54-2] copolymer consists of the following two repeating units



Orthoesters,  $RC(OR^1)_3$  (1), thioesters,  $RCSOR^1$  (2,3) (see SULFUR COMPOUNDS; THIOLS), and carbamates (qv),  $H_2NCOOR$ , are not covered in this review.

### Nomenclature

The names of esters consist of two words that reflect their formation from an alcohol and a carboxylic acid. According to the IUPAC rule, the alkyl or aryl group of the alcohol is cited first followed by the carboxylate group of the acid with the ending -ate replacing the -ic of the acid (4,5). For example,  $\text{CH}_3\text{CH}_2\text{COOCH}_3$ , the methyl ester of propanoic acid, is called methyl propanoate [554-12-1] (or methyl propionate, if the trivial name, propionic acid, is used for the carboxylic acid). The monoesters of dibasic acids are named by inserting the word hydrogen between names of the alcohol and the carboxylate. The monomethyl ester of succinic acid,  $\text{CH}_3\text{OCOCH}_2\text{CH}_2\text{COOH}$ , is called methyl hydrogen succinate or more systematically methyl hydrogen butanedioate [3878-55-5].

Based on the IUPAC rule, esters of polyhydric alcohols with monobasic acids are named analogously to simple esters: 1,2-ethanediyl diacetate for ethylene glycol diacetate [111-55-7], 2-hydroxyethyl acetate for ethylene glycol monoacetate [542-59-6], 1,2,3-propanetriyl triacetate for glycerol triacetate [102-76-1]. Cyclic esters are called lactones, and are named by changing the -ic acid of the hydroxyacid to -lactone. A Greek letter ( $\alpha, \beta, \gamma, \delta$ , etc) is used to designate the carbon atom that bears the hydroxyl group of the parent acid. Lactones are best named, how-

ever, as heterocyclic compounds. For example,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$ ,  $\gamma$ -butyrolactone, is dihydro-2(3H)-furanone [96-48-0].

When the ester function is named as a substituent, it is indicated by alkoxy carbonyl or acyloxy depending on the connection to the  $\text{—C=O}$  group:

$\text{CH}_3\text{OC—R}$  is a methoxycarbonyl derivative whereas  $\text{CH}_3\text{CO—R}$  is the acetoxy derivative. In naming esters containing one or more substituents, it is necessary to indicate specifically in which portion of the molecule the substituents occur, eg,  $\text{ClCH}_2\text{COOCH}_2\text{CH}_3$  is ethyl chloroacetate [105-39-5] and  $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{Cl}$  is 2-chloroethyl acetate [542-58-5].

Orthoesters are trivially named as derivatives of ortho acids such as triethyl orthoformate [122-51-0],  $\text{HC(OC}_2\text{H}_5)_3$ , or named systematically as ethers, 1,1,1-triethoxymethane.

### Physical Properties

The physical properties of organic esters vary according to the molecular weight of each component (6-10). Lower molecular weight esters are colorless, mobile, and highly volatile liquids that usually have pleasant odors. As the molecular weight increases, volatility decreases and the consistency becomes waxy, then solid, and eventually even brittle, often with formation of lustrous crystals. The melting point of an ester is generally lower than that of the corresponding carboxylic acid. However, the boiling point depends on the chain length of the alcohol component and eventually exceeds that of the acid. Lower molecular weight esters are relatively stable when dry and can be distilled without decomposition. Organic esters are generally insoluble in water, but soluble in various organic liquids. Lower esters are themselves good solvents for many organic compounds. The

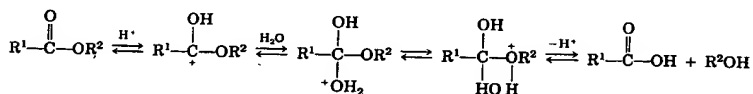
physical properties of commercially important aliphatic and aromatic organic esters are listed in Table 1.

### Chemical Properties

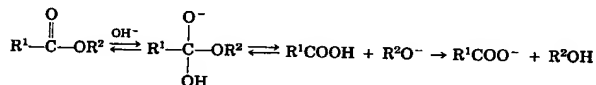
The reactions of esters have been reviewed (11–15). Because of the large number of possible acid and alcohol moieties, the chemical properties of esters may differ considerably. Only typical reactions applicable to the majority of esters are described in the following sections.

**Hydrolysis.** Esters are cleaved (hydrolyzed) into an acid and an alcohol through the action of water. This hydrolysis is catalyzed by acids or bases. The mechanistic aspects of ester hydrolysis have received considerable attention and have been reviewed (16). For most esters only two reaction pathways are important. Both mechanisms involve a tetrahedral intermediate and addition–elimination reactions:

#### Acid



#### Base



Hydrolysis reactions involving tetrahedral intermediates are subject to steric and electronic effects. Electron-withdrawing substituents facilitate, but electron-donating and bulky substituents retard basic hydrolysis. Steric effects in acid-catalyzed hydrolysis are similar to those in base-catalyzed hydrolysis, but electronic effects are much less important in acid-catalyzed reactions. Higher temperatures also accelerate the reaction.

The catalysis of ester hydrolysis by other groups within the ester molecule (intramolecular catalysis) has been extensively studied (17,18). These reactions are important because they simulate catalysis by enzymes. Intramolecular catalysis of esters has been used as a model in drug discovery efforts (19).

**Basic Hydrolysis.** Throughout most of history, soap was manufactured by boiling an ester with aqueous alkali. In this reaction, known as saponification, the ester is hydrolyzed with a stoichiometric amount of alkali. The irreversible formation of carboxylate anion drives the reaction to completion.

**Acidic Hydrolysis.** Hydrolysis of esters by use of water and a mineral acid leads to an equilibrium mixture of ester, alcohol, and free carboxylic acid. Complete reaction can only be achieved by removal of alcohol or acid from the equilibrium. Because esters have poor solubility in water, the reaction rate in dilute

Table 1. Physical Properties of Some Common Esters

Ester	CAS Registry Number	Mol wt	$n_D^{20}$	$d_4^{20}$	Bp, °C <sup>a</sup>	Freezing point, °C	Flash point, °C <sup>b</sup>
methyl formate	[107-31-3]	60.05	1.344	0.0975	32	-99.8	-19
ethyl formate	[109-94-4]	74.08	1.3598	0.9236	54.3	-80	-20
butyl formate	[592-84-7]	102.13	1.3889	0.8885 <sup>c</sup>	106	-91.9	-18
methyl acetate	[79-20-9]	74.08	1.3594	0.933	57	-98.1	-10
ethyl acetate	[141-78-6]	88.1	1.3723	0.0902	77.1	-83.6	-4
vinyl acetate	[108-05-4]	86.1	1.3959	0.932	72.2	-93.2	-8
propyl acetate	[109-60-4]	102.13	1.3844	0.887	101.6	-92.5	13
isopropyl acetate	[108-21-4]	102.13	1.3773	0.872	90	-73.4	2
butyl acetate	[123-86-4]	116.16	1.3951	0.882	126	-73.5	22
isobutyl acetate	[110-19-0]	116.16	1.3902	0.871	117.2	-98.6	18
sec-butyl acetate	[105-46-4]	116.16	1.3877	0.8758 <sup>d</sup>	112		31.1 <sup>e</sup>
t-butyl acetate	[540-88-5]	116.16	1.3855	0.8665 <sup>c</sup>	97		
pentyl acetate	[628-63-7]	130.18	1.4023	0.876	149.3	-70.8	25
isoamyl acetate	[123-92-2]	130.18	1.4000	0.872	142	-78	25
sec-hexyl acetate	[108-84-9]	144.22	1.4014 <sup>f</sup>	0.8651 <sup>g</sup>	157	0	
2-ethylhexyl acetate	[103-09-3]	172.26	1.4204	0.873	199.3	-93	71
ethylene glycol diacetate	[111-55-7]	146.14	1.415	1.128	191	-31	88
2-methoxyethyl acetate	[110-49-6]	118.13	1.4019	1.0067	145	-65.1	44
2-ethoxyethyl acetate	[111-15-9]	132.16	1.4058	0.975	156.4	-61.7	47
2-butoxyethyl acetate	[112-07-2]	160.12	1.42	0.943	187.8	-32	81
2-(2-ethoxyethoxy)ethyl acetate	[111-90-0]	176.21	1.423	1.011	217.4	-25	107
2-(2-butoxyethoxy)ethyl acetate	[112-34-5]	204.27	1.4265	0.981	247	-32.2	110
benzyl acetate	[140-11-4]	150.18	1.5232	1.055	215.5	-51.5	90
glyceryl triacetate	[102-76-1]	218.23	1.4296	1.161	258	-78	138
ethyl 3-ethoxypropionate	[763-69-9]	146.19		0.95	165-172	-50	58
glyceryl tripropionate	[139-46-7]	260.3	1.4318	1.100 <sup>h</sup>	176	-58	167 <sup>e</sup>
methyl acrylate	[96-33-3]	86.09	1.4040	0.953	80.5	< -75	-3
ethyl acrylate	[140-88-5]	100.11	1.4068	0.923	99.8	< -72	10
butyl acrylate	[141-32-2]	128.17	1.4185	0.898	69	-64.6	29
2-ethylhexyl acrylate	[103-11-7]	184.28		0.887	130 <sup>i</sup>	-90	82 <sup>e</sup>

methyl methacrylate	[80-62-6]	100.12	1.4119	0.944	100	-48	10*
methyl butyrate	[623-42-7]	102.13	1.3878	0.898	102.3	-84.8	14
ethyl butyrate	[105-54-4]	116.16	1.4000	0.878	121.6	-100.8	24
butyl butyrate	[109-21-7]	144.22	1.4075	0.871	166.6	-91.5	53
methyl isobutyrate	[547-63-7]	102.13	1.3840	0.891	92.6	-84.7	
ethyl isobutyrate	[97-62-1]	116.16	1.3870	0.869	110	-88	<21
isobutyl isobutyrate	[97-85-8]	144.22	1.3999	0.875	148.7	-80.7	38
methyl stearate	[112-61-8]	298.5	1.457	0.836	215	40	153
ethyl stearate	[111-61-5]	312.52	1.429	1.057	213-215	33.7	
butyl stearate	[123-95-5]	340.58		0.855	343	27.5	160
dodecyl stearate	[5303-25-3]	440.8	1.433			28	
hexadecyl stearate	[1190-63-2]	496.91	1.441			57	
dimethyl maleate	[624-48-6]	144.13	1.4409	1.152	204		91
dimethyl oxalate	[95-92-1]	111.09	1.4096	1.148	185	-41	76
dimethyl adipate	[627-93-0]	174.2	1.4283	1.0600	115	10.3	
diethyl adipate	[141-28-6]	202.25	1.4372	1.008	245	-19.8	
di(2-ethylhexyl) adipate	[103-23-1]	370.58	1.4472	0.927	214	-60	206
methyl benzoate	[93-58-3]	136.15	1.517	1.094	199.5	-12.5	83
ethyl benzoate	[93-89-0]	150.18	1.505	1.051	212.9	-34.2	88
methyl salicylate	[119-36-8]	152.15	1.536	1.184	223.3	-8.6	96
ethyl salicylate	[118-61-6]	166.18	1.522	1.137	231.5	1.3	107
dimethyl phthalate	[131-11-3]	194.19	1.515	1.190	282	-2	146
diethyl phthalate	[84-86-2]	222.24	1.499	1.118	295	-33	161
dibutyl phthalate	[84-74-2]	278.35	1.4911	1.0465	340	-35	157
di(2-ethylhexyl) phthalate	[117-81-7]	390.56	1.486	0.9861	231 <sup>j</sup>	-50	218.3
dimethyl isophthalate	[1459-33-4]	194.19	1.5168	1.194 <sup>c</sup>	124	67	138
dimethyl terephthalate	[120-61-6]	194.19			288	140	153
methyl anthranilate	[134-20-3]	151.17	1.584	1.168	132	24	>100
benzyl cinnamate	[103-41-3]	238.29		1.109 <sup>g</sup>	244 <sup>j</sup>	39	110
dimethyl carbonate	[616-38-6]	90.08	1.3682	1.0694 <sup>c</sup>	90	3	19*
diethyl carbonate	[105-58-8]	118.13	1.3854	0.9752 <sup>c</sup>	127	-43	25

\*At 101.3 kPa = 760 mm Hg unless otherwise stated. <sup>b</sup>Closed cup determination unless otherwise stated. <sup>c</sup> $d_{4}^{20}$  <sup>d</sup> $d_{4}^{15}$   
<sup>g</sup> $n_D^{20}$  <sup>h</sup> $n_D^{20}$  <sup>i</sup> $n_D^{20}$  <sup>j</sup>At 6.7 kPa (50 mm Hg). <sup>k</sup>At 0.67 kPa (5 mm Hg).  
<sup>l</sup>Open cup determination.

acids is fairly low. Therefore, emulsifiers such as sulfonated oleic acid or sulfonated aromatic compounds (Twitchell reagent) are added to facilitate the reaction.

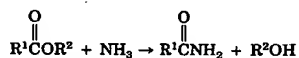
**Hydrolysis by Steam.** High pressure steam, 4.5–5.0 MPa (650–725 psi), at 250°C in the absence of a catalyst hydrolyzes oils and fats to the fatty acids and glycerol (20). The reaction is commonly carried out continuously in a countercurrent method. The glycerol produced during the reaction is continuously extracted from the equilibrium mixture with water. A yield of 98% can be achieved. Currently, the preferred method to produce soaps is steam hydrolysis of fats followed by alkali neutralization of the fatty acids.

**Enzymatic Hydrolysis.** Enzymatic hydrolysis has received enormous attention (21–24). The enzymes generally employed are lipases from microorganisms, plants, or mammalian liver. They effect hydrolysis below 40°C. However, this temperature limit can be raised by employing the enzymes from thermophilic bacteria. The enzymes may be used as a crude extract, in purified form or entrapped on a solid support. The great advantage of the enzymatic process is its high chemo- and stereoselectivity. Enzymatic hydrolysis has been used to effect partial hydrolysis of triglycerides, chiral separations of racemic esters, and selective production of specific fatty acids from fats (25). For example, lipase from *Candida cylindracea* was employed to resolve racemic mixtures of *R*- and *S*- $\alpha$ -methylarylacetic acid esters to yield *S*- $\alpha$ -methylarylacetic acids (26).

**Transesterification.** When esters are heated with alcohols, acids, or other esters in the presence of a catalyst, the alcohol or acid groups are exchanged. This process is called transesterification. It is accelerated by the presence of a small amount of acid or alkali. Three types of transesterification are known: (1) exchange of alcohol groups (alcoholysis), (2) exchange of acid groups (acidolysis), and (3) ester–ester interchange (see ESTERIFICATION). Alcoholysis and acidolysis are important for preparative purposes. All three are equilibrium reactions and proceed to completion if one component is removed from the reaction mixture, eg, by distillation. Dispersed alkali metals, mainly sodium, alkali metal oxides, and tin salts, are suitable catalysts for the transesterification of fats. Recently, organic titanates have also been used (27). Enzymes can be used as asymmetric catalysts in these reactions to prepare optically active alcohols and esters (28).

Transesterification has a number of important commercial uses. Methyl esters of fatty acids are produced from fats and oils. Transesterification is also the basis of recycling technology to break up poly(ethylene terephthalate) [25038-59-9] to monomer for reuse (29) (see RECYCLING, PLASTICS). Because vinyl alcohol does not exist, poly(vinyl alcohol) [9002-89-5] is produced commercially by base-catalyzed alcoholysis of poly(vinyl acetate) [9003-20-7] (see VINYL POLYMERS). An industrial example of acidolysis is the reaction of poly(vinyl acetate) with butyric acid to form poly(vinyl butyrate) [24991-31-9].

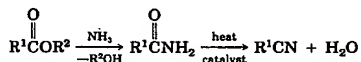
**Ammonolysis and Aminolysis.** Esters and ammonia react to form amides and alcohols:



This reaction can be carried out in aqueous or alcoholic ammonia. Lower mol wt esters give good yields even at room temperature; higher mol wt esters require higher temperature and pressure.

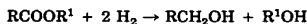
If primary or secondary amines are used, *N*-substituted amides are formed. This reaction is called aminolysis. Hydrazines yield the corresponding hydrazides, which can then be treated with nitrous acid to form the azides used in the Curtius rearrangement. Hydroxylamines give hydroxamic acids.

When esters are passed with ammonia over a contact catalyst such as alumina or thoria at 400–500°C, nitriles are obtained via dehydration of the intermediate amides:



Thus fats are converted to the fatty nitriles (30).

**Reduction.** Esters can be reduced to alcohols by catalytic hydrogenation using molecular hydrogen or by chemical reduction:



**Catalytic Hydrogenation.** Esters can be hydrogenated to primary alcohols using a transition-metal catalyst (31–33) such as copper chromite, copper oxide, Raney nickel, nickel–copper–aluminum–rhenium oxides, or related species. The catalyst of choice is copper chromite. Conditions are stringent: 10–30 MPa (1450–4350 psi) at 150–300°C. Halogens and sulfur are catalyst poisons. When the ester is aliphatic and saturated, the reaction is facile and almost quantitative. Catalysts containing Zn or Cd salts have been developed to convert unsaturated fatty esters into unsaturated fatty alcohols (33,34). The reduction of aromatic carboxylic acid esters proceeds beyond the alcohol in some instances. Benzylic C–O hydrogenolysis, eg, benzyl alcohol to toluene, and aromatic ring hydrogenation upon phenol ester reduction are frequent problems. These problems can be minimized by carrying out the reaction at low temperatures with a high ratio of catalyst to ester.

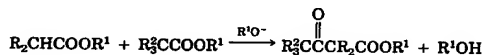
The catalytic hydrogenation of esters is of great commercial importance. It is one of the industrial methods used to produce long-chain fatty alcohols (eg, dodecyl and decyl alcohols) from fatty acid methyl esters (33). The method is also suitable for the conversion of dimethyl 1,4-cyclohexanedicarboxylate [94-60-0] into 1,4-cyclohexanedimethanol [105-08-8], an important intermediate in the manufacturing of polyesters.

**Reduction with Metals and Metal Hydrides.** Practically any ester can be reduced by Na–C<sub>2</sub>H<sub>5</sub>OH, Li or Na–NH<sub>3</sub>, LiAlH<sub>4</sub>, LiBH<sub>4</sub>, or NaBH<sub>4</sub> to give alcohols in excellent yield (35,36). Carbon–carbon double bonds are usually preserved using these reducing reagents.

The reduction of esters to aldehydes is carried out with hydrides such as NaH<sub>2</sub>Al(OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>)<sub>2</sub>, (i-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>AlH, NaAlH<sub>4</sub>, or LiAlH<sub>4</sub>–(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH. The use of BH<sub>3</sub> or LiAlH<sub>4</sub>–BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> as a reducing reagent converts esters to ethers. Thus, reduction of esters can be manipulated by the judicious selection of metal-containing reducing reagents.

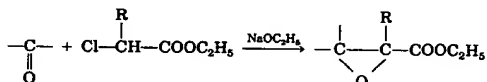
**Reaction of Enolate Anions.** In the presence of certain bases, eg, sodium alkoxide, an ester having a hydrogen on the α-carbon atom undergoes a wide variety of characteristic enolate reactions. Mechanistically, the base removes a

proton from the  $\alpha$ -carbon, giving an enolate that then can react with an electrophile. Depending on the final product, the base may be consumed stoichiometrically or may function as a catalyst. For example, the sodium alkoxide used in the Claisen condensation is a catalyst:



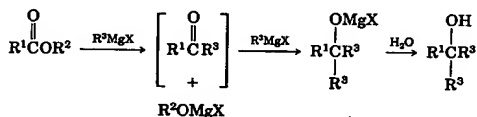
The intramolecular Claisen condensation of diesters, or Dieckman reaction, occurs readily to give five- or six-membered rings, and it has been extensively used for cyclopentanone and cyclohexanone derivatives.

Condensations of aldehydes or ketones with  $\alpha$ -halo esters give  $\alpha,\beta$ -epoxy esters. This is called the Darzens condensation.



The lithium enolate generated using lithium diisopropylamide [4111-54-0], lithium 2,2,6,6-tetramethylpiperidide [38227-87-1], or lithium hexamethyldisilazide [4039-32-1] is a chemical reagent that reacts with other reactants to give a variety of products (37). In the quest for improved stereospecificity, enolates with different cations such as silicon, aluminum, boron, and zinc have also been used (38). In group transfer polymerization, ketene silyl acetals, eg,  $(\text{CH}_3)_2\text{C}=\text{C}(\text{OSi}(\text{CH}_3)_3)(\text{OCH}_3)$  are employed as initiators (39).

**Grignard and Related Reactions.** Esters react with alkyl magnesium halides in a two-stage process to give alcohols:

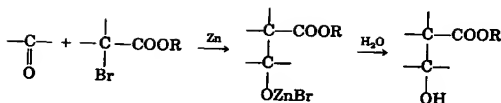


The reaction involves nucleophilic substitution of  $\text{R}^3$  for  $\text{OR}^2$  and addition of  $\text{R}^3\text{MgX}$  to the carbonyl group. With 1,4-dimagnesium compounds, esters are converted to cyclopentanols (40). Lactones react with Grignard reagents and give diols as products.

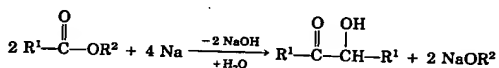
Many other organometallic compounds also react with carbonyl groups. Lithium alkyls and aryls add to the ester carbonyl group to give either an alcohol or an olefin. Lithium dimethylcuprate has been used to prepare ketones from esters (41). Tebbe's reagent,  $\text{Cp}_2\text{TiCH}_2\text{AlCl}(\text{CH}_3)_2$ , where  $\text{Cp}$  = cyclopentadienyl, and other metal carbene complexes can convert the  $\text{C}=\text{O}$  of esters to  $\text{C}=\text{CR}_2$  (42,43).

$\alpha$ -Halo esters react with aldehydes or ketones in the presence of zinc to form  $\beta$ -hydroxy esters. This is known as the Reformatsky reaction (44).



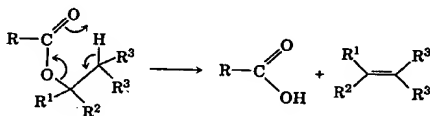


**Preparation of Acyloins.** When aliphatic esters are allowed to react with metallic sodium, potassium, or sodium-potassium alloy in inert solvents, acyloins ( $\alpha$ -hydroxyketones) are formed (45):

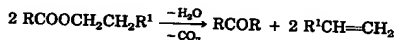


This reaction is used in the synthesis of large-ring compounds.

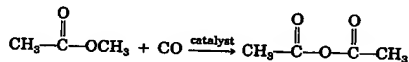
**Pyrolysis.** The pyrolysis of simple esters of the formula  $\text{RCOOCR}^1\text{R}^2\text{CHR}^3_2$  to form the free acid and an alkene is a general reaction that is used for producing olefins:



The pyrolysis is generally carried out at 300–500°C over an inert heat-transfer agent such as Pyrex glass or 96% silica glass chips. Esters of tertiary alcohols are pyrolyzed more readily than esters of secondary alcohols, and esters of primary alcohols are the most difficult to pyrolyze. A detailed review on this reaction has been given (46). However, when heated to high temperatures in the presence of metal oxides such as thorium oxide, calcium oxide, manganese chromite, or zinc chromite, esters of primary alcohols give high yields of ketones (47):

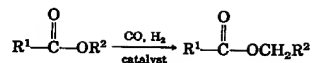


**Carbonylation Reaction.** The carbonylation of methyl acetate is an important industrial reaction for producing acetic anhydride:

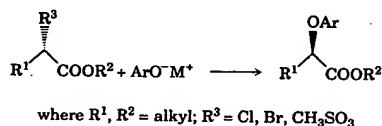


Earlier catalysts were based on cobalt, iron, and nickel. However, recent catalytic systems involve rhodium compounds promoted by methyl iodide and lithium iodide (48,49). Higher mol wt alkyl esters do not show any particular ability to undergo carbonylation to anhydrides.

Ruthenium complexes have been used in the hydrocarbonylation of simple esters to produce the corresponding homologous esters (50). The hydrocarbonylation affects the alkyl moiety rather than the carboxylate group:



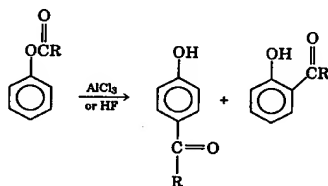
**Substitution, Alkylation, and Rearrangement.** The reaction of alkaline phenoxides with alkyl *S*-2-(chloro)- or *S*-2-(mesyloxy)propionate gives optically active *R*-2-aryloxyalkanoic acid esters in good chemical and optical yields (>97% ee) (51-53):



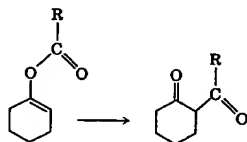
The reaction is utilized in the synthesis of several phenoxy herbicides.

Optically active 2-arylalkanoic acid esters have been prepared by Friedel-Crafts alkylation of arenes with optically active esters, such as methyl *S*-2-(chlorosulfonyl)- or *S*-2-(mesyloxy)propionate, in the presence of aluminum chloride (54,55).

The Fries rearrangement of phenol esters gives a mixture of 2- and 4-acylphenols (56). The reaction is catalyzed by Lewis acids such as aluminum chloride or by Brønsted acids like hydrogen fluoride. This reaction is used in the production of 4-hydroxyacetophenone [99-93-4], a raw material for acetaminophen [103-90-3] (57):



Similarly, enol esters undergo rearrangement to give the corresponding 1,3-diketones. This reaction can be accomplished thermally (500°C) or with a catalyst (58,59):



### Occurrence and Preparation

Currently, most of the simple esters used commercially are of synthetic origin, although esters occur naturally in large quantities in fats, oils, and waxes. Fats and oils from plants and animals consist mainly of glycerol esters of stearic, palmitic, and oleic acids (60). Natural waxes are esters of monobasic carboxylic acids with higher monohydric and, less commonly, dihydric alcohols. Microorganisms produce a complex array of compounds containing the ester linkage, ranging from simple esters to macrocyclic lactones, such as erythromycin, which are important because of their antibacterial properties.

Essential oils are obtained from fruits and flowers (61,62). Volatile esters of short- and medium-chain carboxylic acids or aromatic carboxylic acids with short- and medium-chain alcohols are primary constituents of essential oils, eg, ethyl acetate in wines, brandy, and in fruits such as pineapple; benzyl acetate in jasmine and gardenia; methyl salicylate in oils of wintergreen and sweet birch. Most of these naturally occurring esters in essential oils have pleasant odors, and either they or their synthetic counterparts are used in the confectionery, beverage, perfume, cosmetic, and soap industries (see OILS, ESSENTIAL).

Recovery of naturally occurring esters is accomplished by steam distillation, extraction, pressing, or by a combination of these processes. Synthetic esters are generally prepared by reaction of an alcohol with an organic acid in the presence of a catalyst such as sulfuric acid, *p*-toluenesulfonic acid, or methanesulfonic acid. Ion-exchange resins of the sulfonic acid type can also be used, and an azeotroping agent such as benzene, toluene, or cyclohexane can be used to remove water and force the reaction to completion (see ESTERIFICATION).

### Analysis, Specifications, and Standards

Esters are often characterized by their physical properties. These include boiling point, freezing point, melting point, density, refractive index, residue or ash content, color, odor, and solubility. An overview of the different analytical methods used on organic esters has been written (63). The most common analytical method is the determination of the saponification value, ie, the number of milligrams of KOH necessary to hydrolyze 1.0 g of ester (64,65). Unsaturated esters, eg, natural fats and oils, are often sufficiently characterized by their iodine value. The iodine value is a measure of the number of double bonds in the molecule.

Standard analytical methods and techniques have been developed for the testing of organic esters and determination of specifications. Some of these specifications and the appropriate ASTM methods of analysis include distillation range (ASTM D1078-86), acidity (ASTM D1613-85), color (ASTM D1209-84), non-volatile material (ASTM D1353-90), odor (ASTM D1296-84), purity (ASTM D3362-84), and water (ASTM D1364-90) and alcohol content (ASTM D3545-90).

Many chromatographic methods are applicable to organic ester analysis. Liquid chromatography, both normal and reverse phase, is used for all types of esters. Thin-layer and gas-liquid chromatography have been used for analysis of long-chain alkyl esters (waxes) and acrylates (66,67). If enantiomeric resolution is desired, then specialized stationary phases can be used with gas or liquid chromatography (68). Gas chromatographic and gas chromatographic-mass spectral

methods of detection are required by the United States Government for monitoring and detection of some organic esters (69).

Esters are usually readily identified by their spectroscopic properties (70). Among these, infrared spectroscopy (ir) is especially useful for identifying the carbonyl of the ester group that has characteristic absorption bands. The C=O absorption is very strong in the ir at  $1750\text{--}1735\text{ cm}^{-1}$ ; in addition, C—O stretching bands are observed in the range of  $1100\text{--}1300\text{ cm}^{-1}$ . Another spectroscopic method used in identifying organic esters is nuclear magnetic resonance (nmr). The  $^1\text{H}$  nmr spectra of esters are characteristic for those protons alpha to the carbonyl group. The peaks for these protons show chemical shifts relative to tetramethylsilane [75-76-3] (TMS) between  $\delta$  1.8–2.5 ppm. The peaks for protons alpha to the oxygen function appear between  $\delta$  3.3–4.0 ppm relative to TMS. Typical chemical shifts for olefinic protons of  $\alpha,\beta$ -unsaturated esters and enol esters are between 4.5 and 7.5 ppm down field from TMS. The CH proton of formates gives a signal at about 8.0 ppm down field from TMS, and formate esters are therefore easily identified. Another diagnostic method is  $^{13}\text{C}$  nmr spectroscopy (71,72) which is effective for the detection of ester groups since the  $^{13}\text{C}$  resonance assignable to the carbonyl carbon of the ester group is observable in the range 160–180 ppm downfield from TMS, and is usually distinguishable from other types of carbonyl carbon atoms. Another useful method for ester determination is mass spectroscopy. The mass spectroscopy of esters (73) has been extensively investigated, and a number of general fragmentation processes have been recognized that may be useful for structure determination.

### Stability and Storage

All organic esters are unstable in the presence of acid or base and nucleophiles such as water or alcohols. However, if stored anhydrous, they are stable. Storage vessels can be constructed of steel, aluminum, or other metallic materials, but plastic storage tanks are unsuitable because the highly lipophilic esters can sometimes permeate into the container boundary and soften or even dissolve it. When esters are stored in tanks, a nitrogen blanket and vent are necessary because of potential fire hazards. However, acrylates should be stored in the presence of sufficient oxygen to enable the inhibitor to be effective in preventing polymerization. The esters with high melting points can be stored in paper or wood containers. Proper placarding, packaging, and labeling should always be used before transporting organic esters (74). Sometimes special precautions such as adding inhibitors must be taken before transporting polymerizable esters such as methyl acrylate (75).

The properties of flash point, autoignition temperature, and flammable limit should be considered when an ester is to be handled in any fashion. The flash point is the temperature at which a liquid gives off enough vapor to form an ignitable mixture with air. The flammable limits are the concentrations in air beyond which propagation of flame cannot occur. These limits are usually given as upper and lower concentrations. If the volume percent of the substance is kept above or below these limits, then the mixture will not sustain a flame in oxidizing atmospheres such as air. The autoignition temperature is the temperature required to enable self-sustained combustion of a substance. This information for

some selected organic esters is given in Table 2 along with the NFPA ratings of health, flammability, and reactivity. The NFPA ratings are issued on a scale from 1 to 4, the higher value indicating the highest degree of flammability, toxicity, or reactivity.

If an organic ester is released, then appropriate action must be taken. The United States Department of Transportation has recommendations for responding to such an event. This includes treating the released material as flammable and poisonous if inhaled or absorbed through the skin. Another recommendation is to be aware that combustion may produce irritating or poisonous gases, thus requiring a positive pressure self-contained breathing apparatus to be worn if exposure is possible. Finally, for fighting fires containing organic esters, dry chemical,  $\text{CO}_2$ , water spray, or alcohol-resistant foam extinguishing media should be used (77).

### Health and Safety Factors

**Toxicity.** The degree of toxicity of organic esters covers a wide range (78). These toxicities are usually described in terms of threshold limiting values (TLV), or permissible exposure limits (PEL). Both the PEL and the TLV describe the average concentration over an 8-h period to which a worker may be exposed without adverse effects (79). The PEL and TLV data are often interchangeable, although OSHA uses the PEL values (Table 2). The lethal dosages for 50% of the exposed animals,  $\text{LD}_{50}$ s, are also used as an indicator of the relative toxicity. An accumulation of the  $\text{LD}_{50}$  data of organic esters for rabbits, rats, and mice can also be found in Table 2. The  $\text{LD}_{50}$ s of organic esters for small mammals range between 0.4 and 16 g/kg. The TLVs of organic esters range between 5 and 400 ppm.

When ingested or absorbed, organic esters are likely to be hydrolyzed to the corresponding alcohols and carboxylic acids. Therefore the toxicities of the hydrolysis products should also be considered (80,81). Some organic esters are highly volatile and can act as asphyxiant or narcotic. Also, skin absorption and inhalation are among the hazards associated with esters that are volatile or have good solvent action. Because of the high solubility of fats and oils in organic esters, prolonged or repeated exposure to skin can cause drying and irritation.

Formate esters generally become less toxic as the alcohol moiety increases up to  $\text{C}_4$ . With this increase in alkyl size, the  $\text{LD}_{50}$  (oral, rabbit) increases from 1.62 g/kg for methyl formate to 3.0 g/kg for isoamyl formate [110-45-2]. In comparison, both allyl and vinyl formates are more toxic than their saturated analogues.

Acetates generally do not cause any physiological effects unless high exposure occurs since they are usually converted into or occur naturally as metabolites. However, large enough exposure to acetate esters can cause narcotic effects. The aromatic acetate esters cause death more rapidly than aliphatic acetates with oral  $\text{LD}_{50}$ s (rat) ranging between 2.5 and 1.6 g/kg for phenyl and benzyl acetate compared to  $\text{LD}_{50}$ s (rat) of 4.8 to 8.3 g/kg for methyl through propyl acetate. Vinyl acetate gives approximately the same level of toxicity as the other acetate esters and less so when it is polymerized.

Table 2. Flammability and Toxicity of Organic Esters

Ester	Auto-ignition temp, °C <sup>a</sup>	Upper flammable limit, vol % in air <sup>b</sup>	Lower flammable limit, vol % in air <sup>b</sup>	NFPA <sup>c</sup> hazard information toxicity data						
				Health	Flamma- bility	Reacti- vity	Species	Oral LD <sub>50</sub> , g/kg	PEL <sup>d</sup> , ppm	PEL <sup>d</sup> , mg/m <sup>3</sup>
methyl formate	449	23	4.5	2	4	0	rabbit	1,622	100	250
ethyl formate	455	16.0	2.8	2	3	0	rabbit	2,075	100	300
butyl formate	322	8.2	1.7	2	3	0	rabbit	2.66		
methyl acetate	454	16	3.1	1	3	0	rabbit	3.7	200	610
ethyl acetate	426	11.5	2	1	3	0	rabbit	4.97	400	1400
vinyl acetate	402	13.4	2.6	2	3	2	rat	2.92	10	35 <sup>e</sup>
propyl acetate	450	8	1.7(38°C)	1	3	0	rabbit	6.64	200	840
isopropyl acetate	460	8	1.8(38°C)	1	3	0	rabbit	6.95	250	950
butyl acetate	425	7.6	1.7	1	3	0	rat	14	150	710
isobutyl acetate	421	10.5	1.3	1	3	0	rabbit	4.8	150	700
sec-butyl acetate	422	9.8	1.7	1	3	0	rabbit		200	950
t-butyl acetate		7.3	1.3						200	950
pentyl acetate	360	1.1	7.5	1	3	0	rat	16.6	100	532 <sup>e</sup>
isoamyl acetate	360	7.5	1(100°C)	1	3	0	rabbit	7.42	100	525
sec-hexyl acetate	266	5	0.9				rat	6.16	50	300
2-ethylhexyl acetate	268	8.14	0.76	2	2	0	rat	>3.2		
ethylene glycol diacetate	482	8.4	1.6	1	1	0	rat	6.86		
2-methoxyethyl acetate	394		1.7	0	2	0	rat	3.39	25	120
2-ethoxyethyl acetate	380	12.7(135°C)	1.7	2	2	0	rat	5.1	5	27 <sup>e</sup>
2-butoxyethyl acetate	340	8.54(135°C)	0.88(93°C)				mouse	1.6		
2-(2-ethoxyethoxy)ethyl acetate	360	23.5(182°C)	0.98(135°C)				rat	8.69		
2-(2-butoxyethoxy)ethyl acetate	290	24.6	0.76(135°C)				rat	11.9		
benzyl acetate	460	6.1	1(189°C)	1	1	0	rat	2.5		
glyceryl triacetate	433	6.4	1.0(189°C)	1	1	0	mouse	1.5 <sup>f</sup>		
glyceryl tripropionate	421		0.8(186°C)	0	1	0	rat	6.4		
ethyl 3-ethoxypropionate	377	8.7	1.05(88°C)				rat	5		
methyl acrylate	468	25	2.8	2	3	2	rat	3	10	35
ethyl acrylate	372	14	1.4	2	3	2	rabbit	1	25	100
butyl acrylate	292	9.9	1.7	2	2	2	rat	3.7	10	52 <sup>e</sup>

252	2-ethylhexyl acrylate	6.4	0.8	2	2	2	2	rat	5.6	100	410
	methyl methacrylate	8.2	1.7	2	3	2	2	rabbit	6.55		
463	methyl butyrate	8.8	1.6	2	3	0	0	rabbit	3.38		
	ethyl butyrate	7.7	1.3	0	3	0	0	rabbit	5.23		
	butyl butyrate	6.1	1	2	2	0	0	rabbit	9.52		
	methyl isobutyrate	9	1.6					rat	16		
	ethyl isobutyrate	7.8	1.3	0	3	0	0	mouse	0.8 <sup>c</sup>		
432	isobutyl isobutyrate	7.59	0.96	0	2	0	0	rat	12.8 <sup>c</sup>		10 <sup>c</sup>
	methyl stearate			0	1	0	0				
355	ethyl stearate	4.9	0.3	1	1	0	0	rat	>32		
	dodecyl stearate										
	hexadecyl stearate										
	dimethyl maleate	10.4	1.6	1	1	0	0	rat	1.41		
	dimethyl oxalate	8.4	1.5	0	2	0	0	rat	0.4-1.6		
	dimethyl adipate							rat	1.81 <sup>f</sup>		
377	diethyl adipate		0.4(242°C)	0	1	0	0	rat	>1.6		
	di(2-ethylhexyl) adipate		1.2	0	2	0	0	rat	9.1		
	methyl benzoate	6.7	1	1	1	0	0	rabbit	2.17		
490	ethyl benzoate	6.1	1.2	1	1	0	0	rabbit	2.63		
454	methyl salicylate	7.2		1	1	0	0	rabbit	2.8		
	ethyl salicylate							rat	1.32		
490	dimethyl phthalate	5.8	0.9(180°C)	0	1	0	0	mouse	7.2 <sup>f</sup>		5
457	diethyl phthalate	5.3	0.7(186°C)	0	1	0	0	rabbit	1		5 <sup>c</sup>
402	diethyl phthalate	5.3	0.5(235°C)	0	1	0	0	rat	8		5 <sup>c</sup>
390	di(2-ethylhexyl) phthalate	5.3	0.3(245°C)	0	1	0	0	rat	>26		5
	dimethyl isophthalate	5.8	1	0	1	0	0	rat	4.39		
518	dimethyl terephthalate	5.5	0.03	1	1	0	0	rat	>3.2		
	methyl anthranilate			0	1	0	0	rat	2.91		
	benzyl cinnamate							rat	5.53		
	dimethyl carbonate							rat	13		
	diethyl carbonate	12.4	1.7	2	3	1	1	mouse	8.5		

<sup>a</sup>ASTM D286 and D2155. <sup>b</sup>ASTM D681 (temperature at which limit was determined). <sup>c</sup>See Ref. 8. <sup>d</sup>Permissible exposure limit, see Ref. 76. <sup>e</sup>Threshold limit value-time-weighted average. <sup>f</sup>Intrapertoneal. <sup>g</sup>LD<sub>100</sub>.

Propionates and higher aliphatic esters generally become less toxic as the size of the alkyl carboxylate increases. As an example, the  $LD_{50}$  (rat, oral) for ethyl nonanoate [123-29-5] is greater than 43 g/kg, and the  $LD_{50}$  (rat, oral) for ethyl heptanoate [106-30-9] is 34.6 g/kg.

The acrylate esters are more physiologically hazardous than their saturated homologues. They are usually lachrymators and irritants, and their toxicities decrease with increasing molecular weights. The  $LD_{50}$ s of acrylates usually fall between 1 and 5 g/kg for rabbits. Methacrylate esters are generally less toxic than their corresponding acrylates. The decreased physiological activity is believed to result from added steric hindrance of the  $\alpha$ -methyl group, but the methacrylates are potent sensitizers.

Among adipates, oxalates, malonates, and succinates, the adipates are the least toxic. An example of this can be seen in the comparison between di(2-ethylhexyl) adipate, which has an oral  $LD_{50}$  rat of 9.1 g/kg, and di(2-ethylhexyl) succinate [117-81-7], which has an oral  $LD_{50}$  rat of 4.3 g/kg. The malonates and oxalates are generally more toxic than the adipates. Exposure to diethyl oxalate [95-92-1], the most common oxalate, gives symptoms similar to exposure to oxalic acid [114-62-7], ie, twitching and convulsions. The malonates presumably are less toxic than oxalates because the corresponding malonic acid sodium and calcium salts are much more soluble than calcium oxalates and are thus more easily excreted.

Benzoate esters, like most organic esters, are not very toxic. They are not absorbed through the skin as rapidly as alkyl esters but are more potent physiologically. They are also moderate skin irritants. The oral  $LD_{50}$ s (mouse) for methyl- to butylhydroxy benzoates range between 8 and 5 g/kg.

The phthalate esters are one of the most widely used classes of organic esters, and fortunately they exhibit low toxicity (82). Because of the ubiquitous nature of phthalates, many investigations have been conducted to determine their toxicities to marine life as well as in mammals (83-85). Generally, phthalates are not absorbed through the skin and are not very potent when inhaled. The phthalates become less toxic as the alcohol group increases in molecular weight. For example, dimethyl phthalate has an oral  $LD_{50}$  (mouse) of 7.2 g/kg, whereas di(2-ethylhexyl) phthalate shows an oral  $LD_{50}$  (rat) of greater than 26 g/kg.

More information on the toxicities of a range of organic esters is available in the literature (86,87).

**Exposure Limits.** The Occupational Safety and Health Act (OSHA) of 1990 lists a multitude of acetates, phthalates, formates, and acrylates along with the corresponding permissible exposure limits and threshold limit values (76). The PEL data is listed in Table 2. If there is potential for exposure to an organic ester for which PEL or TLV data has been identified, then an exposure limit lower than that listed is usually selected for working in that environment.

### Regulation and Waste

Waste from production of organic esters is usually not a problem since the method of synthesis often involves a carboxylic acid condensation with an alcohol and the only by-product is water. Any organic remnants lost to the process water can usually be biologically degraded. The biochemical oxygen demand (BOD) or chem-



ical oxygen demand (COD) should be measured if biological treatment is used on the process waste from ester production (87). Organic ester vapor emitted in processing usually can be burned.

Extensive federal environmental regulations exist that govern organic esters as well as many other substances (88). These regulations must always be consulted for complete information before using large amounts of organic esters (89). State and local regulations must also be met, which in some cases are more stringent than federal regulations.

Among these federal regulations, the Clean Air Act regulates the amount of an organic ester or other substance that is allowed to be emitted into the atmosphere. Several organic esters are listed as Hazardous Air Pollutants in the Clean Air Act amendments of 1990, and therefore are more tightly regulated (90). If an organic ester is sent to a wastewater treatment facility and subsequently discharged to surface waters, then compliance with the Clean Water Act is required (91). If an organic ester or other substance becomes a solid waste as defined under the Resource Conservation and Recovery Act (RCRA), then specific requirements apply that regulate the treatment, storage, and disposal of that waste. Regulations under RCRA and the Department of Transportation also apply that pertain to the proper labeling, manifesting, and shipping of hazardous wastes (92). The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) provides a list of hazardous substances, some of which are organic esters (93). The organic esters listed in CERCLA must be properly reported if spilled or otherwise released to the environment in amounts exceeding the reportable quantities specified. Note that spills or releases may need to be reported to state agencies even in amounts that do not exceed the CERCLA reportable quantity. The Superfund Amendments and Reauthorization Act (SARA) of 1986 established regulations requiring facilities to annually report organic esters and other chemicals stored on-site in amounts exceeding reporting thresholds in pure form or as percentages in mixtures. Facilities must also report certain organic esters and other chemicals (listed under SARA 313) that are stored in amounts exceeding reporting thresholds that are released to the environment via air, water, or off-site disposal (94).

## Uses

Table 3 lists only those carboxylic acid esters whose 1990 U.S. production, sales quantity, value, and raw materials have been published (95). They are grouped on the basis of their principal use. For a complete list of the organic esters produced and sold in the United States and their manufacturers, the original publication should be consulted. Uses of some specific esters are also given in Table 4.

**Solvents.** Lower esters are extensively used as solvents in coatings (eg, paints and top coats on automobiles), inks, and adhesives, and in processing other substances (96). They readily dissolve resins or their precursors to become vehicles for application. Because these solvent esters are not on the list of 189 hazardous air pollutants regulated by Section 112 of the Clean Air Act of 1990, they will not face the decline in use in the short term that methyl ethyl ketone and methyl isobutyl ketone will. However, in the long term, environmental concerns

Table 3. (Continued)

Material	CAS Registry Number	Production, t	Sales	
			Quantity, t	Value, 10 <sup>3</sup> \$
<i>Miscellaneous chemicals</i>				
esters of monohydric alcohols, total		3,113,090	1,481,937	1,354,300
n-butyl acetate	[123-86-4]	114,530	93,242	70,511
butyl acrylate	[141-32-2]	280,129	108,684	129,733
dilauryl-3,3'-thiodipropionate	[123-28-4]	694	704	2,684
distearyl-3,3'-thiodipropionate	[693-36-7]	2,519	2,456	8,168
ethyl acetate (100% basis)	[141-78-6]	123,522	113,668	76,296
ethyl acrylate	[140-88-5]	136,485	66,442	71,791
2-ethylhexyl acrylate	[103-11-7]	53,348	46,300	55,475
fatty acid esters, not included with plasticizers or surface-active agents, total		5,614	2,955	4,904
methyl esters of tallow	[61788-61-2]	2,526		
myristyl myristate	[3234-85-3]		88	607
all other fatty acid esters not included with plasticizers or surface-active agents		3,088	2,867	4,297
isopropyl acetate	[108-21-4]	20,376	19,299	16,970
methyl methacrylate, monomer	[80-62-6]	536,283		
propyl acetate	[109-60-4]	32,868	30,612	29,968
vinyl acetate, monomer	[108-05-4]	1,206,021	674,970	465,772
all other monohydric alcohol esters		471,306	292,578	357,367
polyhydric alcohol esters, total		145,708	128,357	184,527
2-(2-butoxyethoxy)ethyl acetate	[112-34-5]	4,701	2,957	4,476
2-butoxyethyl acetate	[112-07-2]	8,357	6,492	9,709
glycerides, mixed C14-18 and C16-18, mono- and di-		13,863	13,387	16,993
all other polyhydric alcohol esters		118,787	105,521	153,349

enforced by regulations to reduce the amount of volatile organic components (VOCs) in air will gradually decrease the usage of esters in solvent applications.

**Plasticizers.** Plasticizers are materials that soften and flexibilize inherently rigid, and even brittle polymers. Organic esters are widely used as plasticizers in polymers (97,98). These esters include the benzoates, phthalates, terephthalates, and trimellitates, and aliphatic dibasic acid esters. For example, triethylene glycol bis(2-ethylbutyrate) [95-08-9] is a plasticizer for poly(vinyl butyral) [63148-65-2], which is used in laminated safety glass (see VINYL POLYMERS, POLY(VINYL ACETALS)). Di(2-ethylhexyl)phthalate [117-81-7] (DOP) is a preeminent plasticizer. Variation of acid and/or alcohol component(s) modifies the efficacy of the resultant ester as a plasticizer. In phthalate plasticizers, molecular sizes of the alcohol moiety can be varied from methyl to tridecyl to control permanence, compatibility, and efficiency; branched (eg, 2-ethylhexyl, isodecyl) for rapid absorption and fusion; linear (C6-C11) for low temperature flexibility and

**Table . Uses of Some Specific Esters**

Name and structure	Use
methyl formate, $\text{HCOOCH}_3$	raw material for production of formamide, dimethylformamide, and formic acid
methyl acetate, $\text{CH}_3\text{COOCH}_3$	solvent for cellulose nitrate, cellulose acetate, and many resins and oils; used in the manufacture of artificial leather; raw material for production of acetic anhydride via carbonylation
ethyl acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$	primarily as a solvent for various resins in protective coatings; also used extensively in formulating printing inks and adhesives; new applications include its uses as a process solvent in the pharmaceutical industry and as an extraction solvent in food processing; as a substitute <sup>a</sup> for methyl ethyl ketone (MEK) in many applications
propyl acetate, $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$	good solvent for cellulose nitrate, chlorinated rubber, and heat-reactive phenolics; principal use is as a printing ink solvent <sup>b</sup>
isopropyl acetate, $\text{CH}_3\text{COOCH}(\text{CH}_3)_2$	active solvent for many synthetic resins, such as ethylcellulose, cellulose acetate butyrate, cellulose nitrate, some vinyl copolymers, polystyrene, and methacrylate resins; as a solvent for printing ink; like propyl acetate, it can also be used in the recovery of acetic acid from dilute aqueous solutions
butyl acetate, $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{CH}_3$	excellent solvent for inks and lacquers because of its high blush resistance and evaporation rate; widely used as solvent in paints, thinner, video tape binders, and extraction of pharmaceuticals; also used as a perfume ingredient and as a component in synthetic flavors such as apricot, banana, butter, pear, quince, pineapple, grenadine, butterscotch, and raspberry; also a cleaning solvent for silicon wafers
isobutyl acetate, $\text{CH}_3\text{COOCH}_2\text{CH}(\text{CH}_3)_2$	resembles butyl acetate and methyl isobutyl ketone (4-methyl-2-pentanone) and can be used interchangeably for these solvents in many formulations; also a component in synthetic flavors of apple, apricot, banana, butter, mirabelle plum, pineapple, rum, and strawberry
amyl acetates, $\text{CH}_3\text{COOC}_5\text{H}_{11}$	amyl acetate and mixed amyl acetates (a mixture of normal, secondary, and isoamyl acetates) are used as lacquer solvents, as extractants in penicillin manufacture, and in the production of photographic film, leather polishes, dry-cleaning preparations, and flavoring agents; mixed <i>sec</i> -amyl acetates are used as solvents for cellulose compounds and in the production of leather finishes, textile sizes, and printing compounds; isoamyl acetates are used as solvents and in flavorings and perfumes

Table 4. (Continued)

Name and structure	Use
2-ethylhexyl acetate, $\text{CH}_3\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)(\text{CH}_2)_3\text{CH}_3$	high boiling retarder solvent with limited water solubility used to promote flow of and retard blushing in lacquers, emulsions, and silk-screen inks, and as a flow-control agent in baking enamels; also used as a dispersant for vinyl organosols, and as a coalescing aid for latex paints
2-butoxyethyl acetate, $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{OC}_4\text{H}_9$	slow-evaporating glycol ether ester useful as a coalescing aid in poly(vinyl acetate) emulsion system; also used as a retarder solvent in lacquers, enamels, and printing inks
2-(2-butoxyethoxy) ethyl acetate, $\text{CH}_3\text{CO}(\text{OCH}_2\text{CH}_2)_2\text{OC}_4\text{H}_9$	solvent in printing inks and high bake enamels; also used as a coalescing aid in latex paints, in silk-screen inks, and as a component in polystyrene coatings for decals
1-methoxy-2-propyl acetate, <sup>c</sup> $\text{CH}_3\text{CH}(\text{OCOCH}_3)\text{CH}_2\text{OCH}_3$	solvent in inks, ink remover, paints, automotive coatings, and photoresist; also a substitute for 2-ethoxyethyl acetate in many applications
benzyl acetate, $\text{CH}_3\text{COOCH}_2\text{C}_6\text{H}_5$	component of the extract of gardenia, hyacinth, and ylang-ylang, and the main component of extract of jasmine; most benzyl acetate is used in soap odors, but it is also popular for other perfumes and is used to a minor extent in flavors
ethyl 3-ethoxypropionate, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{COOC}_2\text{H}_5$	linear ether ester with excellent solvent properties for many of the polymers and resins used in coating industry; provides lower solution viscosity than many other retarder solvents of similar evaporation rate, and it can be a replacement for 2-ethoxyethyl acetate
isobutyl isobutyrate, $(\text{CH}_3)_2\text{CHCOOCH}_2\text{CH}(\text{CH}_3)_2$	a retarder solvent in wood lacquers, automotive coatings, metal coatings, and a variety of thinner blends; also used in high solids coatings because of its low surface tension, which improves surface characteristics; its distinct odor and flavor make it an interesting material for the formulation of perfumes, and as a bulk component of flavor essences
2,2,4-trimethyl-1,3-pentanediol <sup>d</sup> monoisobutyrate	widely used as a coalescing aid in latex paints, effective with a broad range of latex emulsion systems; retarder solvent for high solid coatings, and a sweetener in letterpress and lithographic inks to improve solvent activity of ink's solvent system
butyl stearate, $\text{CH}_3(\text{CH}_2)_{16}\text{COO}(\text{CH}_2)_3\text{CH}_3$	used for compounding lubricating oils, as a lubricant for the textile and molding trade, in special lacquers, and as a waterproofing agent; in the cosmetic and pharmaceutical fields, it is used in vanishing creams, ointments, rouges, lipsticks, and nail polishes; its oily characteristics have made it of particular value in polishes and coatings that are to be polished

**Table 4. (Continued)**

Name and structure	Use
di(2-ethylhexyl) adipate, $[\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9]_2$	plasticizer to impart low temperature flexibility to PVC formulations, particularly in vinyl meat-wrapping film
benzyl benzoate, $\text{C}_6\text{H}_5\text{COOCH}_2\text{C}_6\text{H}_5$	used in perfumery as a fixative, as a solvent for synthetic musks, and in confectionery and chewing gum flavors; also used in medicine and cosmetics and as plasticizer, insect repellent, and dye carrier
methyl salicylate, $2\text{-OHC}_6\text{H}_4\text{COOCH}_3$	main component of wintergreen oil and occurs in small quantities in other essential oils and fruit; used primarily for the relief of muscular aches, articular rheumatism, and neuralgia; as a flavor and fragrance agent, it is used in confectionery, dentifrices, cosmetics, and in perfumes; also used as a dye carrier and uv light stabilizer in acrylic resins
benzyl salicylate	widely used in soap and cosmetic industry as fragrance; also effective in absorbing uv light, and can be used in protective sunscreen lotions
methyl 4-hydroxybenzoate	broad spectrum of antimicrobial activity, low levels of toxicity, excellent stability and inertness; used as preservative in cosmetic formulations, general-purpose cleaners, disinfectants, and mouth wash and contact lens cleaning solutions; also used as food additive and pharmaceutical preservative
methyl cinnamate, $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOCH}_3$	fragrance in soaps, perfumes, and confectioneries
2-ethylhexyl 4-methoxycinnamate	absorbs uv rays effectively; thus about 75% of all sunscreen formulations use it; usually nonallergenic and nonstaining
dimethyl phthalate	raw material for polyesters; also used as plasticizer, mosquito repellent, dye carrier, and in hair sprays
dimethyl terephthalate	raw material for polyesters such as poly(ethylene terephthalate), poly(butylene terephthalate), and unsaturated polyester
di(2-ethylhexyl) phthalate <sup>a</sup>	plasticizer; also used as an insulating fluid in electrical transformers and pressure-sensitive printing

<sup>a</sup>Ethyl acetate (exempt solvent) is much less toxic than MEK.

<sup>b</sup>Compared with ethyl acetate and isopropyl acetate, propyl acetate has slow evaporation rate and good solvent power which promote improved flow and leveling characteristics in a variety of coating formulations.

<sup>c</sup>Propylene glycol methyl ether acetate.

<sup>d</sup> $(\text{CH}_3)_2\text{CHCOOCH}_2\text{C}(\text{CH}_3)_2\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2$ .

<sup>e</sup>Diocetyl phthalate (DOP).

low volatility; and aromatic (benzyl) for solvating. Terephthalates are recognized for their migration resistance, and trimellitates for their low volatility in plasticizer applications.

**Resins, Plastics, and Coatings.** Unsaturated and difunctional esters are important monomers for the manufacture of many polymers in commercial use. For example, free-radical polymerization of vinyl acetate and methyl methacrylate produces poly(vinyl acetate) [9003-20-7] (PVAc) and poly(methyl methacrylate) [9011-14-7], respectively. Applications of PVAc include latex paint, paper manufacturing, coating for paper board, and adhesives for packaging and labeling (see VINYL POLYMERS, POLY(VINYL ACETATE)). Poly(methyl methacrylate) is used for glazing, lighting fixtures, optical fibers, and surface coatings (see METHACRYLIC POLYMERS). Another example is dimethyl terephthalate (DMT) which reacts with ethylene glycol to yield poly(ethylene terephthalate) [25038-59-9] (PET). PET is used in fibers, films, and bottles (see POLYESTERS). Liquid crystal polymers (LCPs) are a class of thermoplastic polyesters with aromatic carbon backbones. Amoco's Xydar resins are based on terephthalic acid, 4,4'-dihydroxybiphenyl [92-88-6], and 4-hydroxybenzoic acid [99-96-7]. Hoechst Celanese's Vectra resins are based on 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid (see ENGINEERING PLASTICS). LCPs have found application in aviation, electronics (connectors, sockets, chip carriers), automotive underhood parts, and chemical processing. Copolymerization of ethylene with unsaturated esters such as vinyl acetate, methyl acrylate, ethyl acrylate, or butyl acrylate yields polyolefins with special properties. Unsaturated polyesters, produced by condensation of unsaturated dibasic acids (eg, maleic anhydride), and glycols (eg, propylene glycol), are used as thermosets when combined with a cross-linking agent (eg, styrene) in the presence of a free-radical initiator and a promoter. Their applications include boat, automotive exterior parts, cultured marbles, bowling balls, polymeric concrete, and coatings. Polyester polyols are used in polyurethanes (see URETHANE POLYMERS).

Poly(3-hydroxybutyrate-3-hydroxyvalerate) [80181-31-3] resin, produced from a bacterium during a sugar fermentation process, has been reported to be biodegradable, and its target markets include "flushables" such as feminine hygiene products and disposable diapers (99) (see PLASTICS, ENVIRONMENTALLY DEGRADABLE).

**Lubricants.** Monohydric alcohol esters of dibasic acids and polyol esters of monobasic acids are synthetic lubricants (100). They are generally prepared from the following alcohols and acids: (1)  $C_8$ - $C_{13}$  monohydric alcohols such as 2-ethylhexyl, iso-octyl, isodecyl, and isotridecyl alcohols; (2) polymethylol compounds such as trimethylolpropane, pentaerythritol, and dipentaerythritol; (3)  $C_6$ - $C_{10}$  monobasic acids such as heptanoic and nonanoic acids; and (4)  $C_6$ - $C_{10}$  dibasic acids such as adipic, azelaic and sebacic acids, and phthalic anhydride. These esters are mainly used as base oils in high performance lubricants for automotive (eg, engines), aviation (eg, gas turbines), and machinery (eg, gear, chain, and air compressor) industries. Compared with petroleum oils, ester lubricants exhibit lower pour point, higher thermal and oxidation stability, high viscosity index, lower volatility, and better lubricity. For example, bis(2-ethylhexyl) sebacate [122-62-3] is widely used as base oil for lubricating turbojet engines. Polyol esters are used as textile lubricants because of reduced carbon deposit formation.

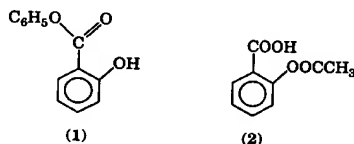
**Perfumes, Flavors, Cosmetics, and Soap.** Many naturally occurring esters in essential oils and some synthetic esters are important fragrance and flavor compounds (61,62). They are used in perfumes, flavors, cosmetics, soaps, detergents, and air fresheners. Benzyl, butyl, ethyl, methyl, and phenyl esters of benzoic acid are used as flavors, perfumes, and food preservatives. Glyceryl 4-aminobenzoate [136-44-7] and 2-ethylhexyl 4-dimethylaminobenzoate [21245-02-3] are used in cosmetic sunscreen preparations. Alkyl esters of 4-hydroxybenzoic acid, called parabens, have been used under various names for fungus infections of the skin, and as preservatives in lotions and creams (101). Soap and cosmetic fragrances use large amounts of amyl and benzyl salicylate. Benzyl salicylate [118-58-1] is also used in deodorant sprays. 2-Ethylhexyl salicylate [118-60-5] and 2-ethylhexyl 4-methoxycinnamate [5466-77-3] are used in sunscreen formulations (102).

Benzyl diethyl[(2,6-xylylcarbamoyl)methyl]ammonium benzoate (denatonium benzoate [3734-33-6], Bitrex) is an extremely bitter tasting, nonirritating, and nonmutagenic compound that has been widely used in many household products such as detergents, nail polish removers, and cleaning agents, to prevent childhood poisoning. It is also used as an alcohol denaturant.

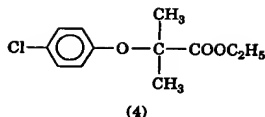
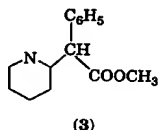
Organic esters in the form of fats and oils from tallow and plants such as soybean, cottonseed, linseed, and castor bean are important raw materials for soap, paints, and food industries.

**Surface-Active Agents.** Polyol (eg, glycerol, sorbitol, sucrose, and propylene glycol) or poly(ethylene oxide) esters of long-chain fatty acids are nonionic surfactants (qv) used in foods, pharmaceuticals, cosmetics, textiles, cleaning compounds, and many other applications (103,104). Those that are most widely used are included in Table 3.

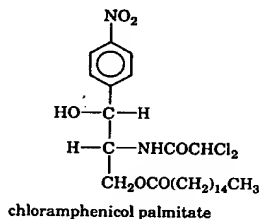
**Medicinals.** Many esters are used as pharmaceuticals (105,106). Of these, benzoic acid, ethyl 4-aminobenzoate [94-09-7] is a topical anesthetic. Phenyl salicylate [118-55-8] (1) has antipyretic, antirheumatic, and antiparasitic properties.



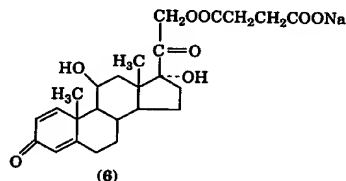
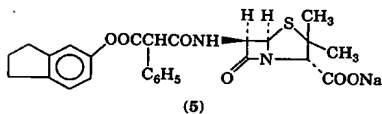
Some simple benzoates are also used as antiseptic agents. Salicylic acid esters are used as antibacterial agents and pain relievers. Analgesic balms, creams, sprays, and nasal inhalers usually contain various combinations of either methyl or menthyl salicylate and menthol. In general, esterification of a physiologically active alcohol or phenol with aliphatic carboxylic acid or an acid with alcohol detoxifies it by decreasing the concentration of active compound present. The active compound is released gradually in the body by hydrolysis of the ester (107). Examples include aspirin [50-78-2] (2), a common analgesic; methyl phenyl salicylate [113-45-1] (3), a central nervous system stimulant; and clofibrate [637-07-0] (4), an antihyperlipoproteinemic.



In recent years, many parent drugs have been converted to esters to generate so-called prodrugs in order to overcome some undesirable property such as bitter taste, poor absorption, poor solubility, and irritation at site of injection. For example, antibiotics such as chloramphenicol [56-75-7] and clindamycin [18323-44-9] have been derivatized as their palmitate esters in order to minimize their bitter taste.



In order to improve the poor oral absorption of carbenicillin [4697-36-3], a lipophilic indanyl ester has been formulated, Geocillin [35531-88-5] (5). Prednisolone [50-24-8], a steroid, is derivatized to its C-21 hemisuccinate sodium salt (6) to make it extremely water-soluble (108).

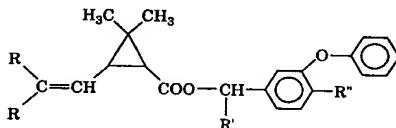
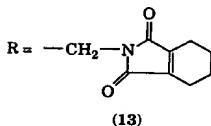
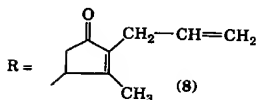
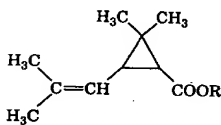
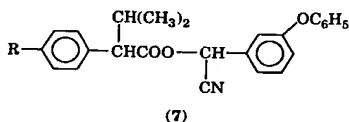


**Herbicides and Pesticides.** Several esters are used as herbicides and pesticides (109-111). Many halogenated benzoic acid esters are phytotoxic and are used as herbicides. Dimethyl tetrachloroterephthalate [1861-32-1] and diisopropyl 5-nitroisophthalate [10552-74-6] are used as herbicide and fungicide, respectively. The phenoxy herbicides are primarily propyl, butyl, and isooctyl esters of 2,4-dichlorophenoxyacetic acid [94-75-7], 4-chloro-2-methylphenoxyacetic acid [93-65-2], and methyl, ethyl, or butyl esters of 2-(4-hydroxyphenoxy)propionic acid [67648-61-7]. Because of their low toxicity, high selectivity, and relatively short life in the soil, phenoxy herbicides are widely used. They are used for controlling



weeds in a large number of grass crops, ie, corn, small grains, sorghum, rice, sugarcane, pasture, range land, and turf.

Pyrethroids are synthetic esters produced to imitate or improve the activity of biological principles of the pyrethrum plant. They are powerful contact insecticides causing rapid knockdown of treated insects. The pyrethroids are extensively used in controlling insect pests on fruit trees, vegetables, and other field crops; in space sprays and contact sprays to kill insects infesting homes, industrial locations, and nonfood processing areas; and in protection of warehoused food. These compounds include fenvalerate [51630-58-1], (7), R = Cl; flucythrinate [70124-77-5], (7), R = CHF<sub>2</sub>O; allethrin [584-79-2] (8); cyfluthrin [68359-37-5] (9); cypermethrin [52315-07-8] (10); deltamethrin [52918-63-5] (11); permethrin [52645-53-1] (12); and tetramethrin [7696-12-0] (13).



- (9) R = Cl; R' = CN; R'' = F  
 (10) R = Cl; R' = CN; R'' = H  
 (11) R = Br; R' = CN; R'' = H  
 (12) R = Cl; R' = H; R'' = H

#### Miscellaneous Uses.

Since esters can be made and hydrolyzed with ease, they are used as protecting groups for hydroxyl and carboxylic acid groups (112). Acetates and benzoates are widely used in carbohydrate, steroid, and nucleoside chemistry, and their cleavage is based on hydrolysis with base, ammonolysis, or methanolysis. Of great importance in peptide chemistry are the *t*-butyl, benzyl, and substituted benzyl esters (113,114). In recent years, esters as protecting groups have played an increasing role in modulating efficacy and bioavailability of pharmaceuticals.

Esters such as benzoates and phthalates are also used in the preparation of high activity catalysts for olefin polymerization. They appear to function as electron donors in the catalyst complex, and play a significant role in catalyst performance (115).

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(54) Hindered-Hydroxyl Functional (Meth)Acrylate-Containing  
Copolymers and Compositions Including Same

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**HINDERED-HYDROXYL FUNCTIONAL (METH)ACRYLATE-  
CONTAINING COPOLYMERS AND COMPOSITIONS  
INCLUDING SAME**

**Abstract**

This invention relates to hindered-hydroxyl functional (meth)acrylate compounds and derivatives thereof and to processes for the preparation thereof. This invention also relates to hindered-hydroxyl functional (meth)acrylate-containing copolymers and to compositions including same. The hindered-hydroxyl functional (meth)acrylate-containing copolymers have utility in coatings, adhesives, inks, sealants, as well as in other end uses.

**HINDERED-HYDROXYL FUNCTIONAL (METH)ACRYLATE-  
CONTAINING COPOLYMERS AND COMPOSITIONS  
INCLUDING SAME**

**Brief Summary of the Invention**

**Technical Field**

This invention relates to hindered-hydroxyl functional (meth)acrylate compounds and derivatives thereof and to processes for the preparation thereof. The hindered-hydroxyl functional (meth)acrylate compounds are useful as copolymerizable monomers in various polymerization methods. This invention also relates to hindered-hydroxyl functional (meth)acrylate-containing copolymers and to compositions including same. The hindered-hydroxyl functional (meth)acrylate-containing copolymers are useful in preparing coatings, adhesives, inks and sealants that can be cured with a variety of crosslinking agents.

**Background of the Invention**

Although (meth)acrylic coatings are known to have very good weathering characteristics, they are subject to deterioration by etching under both high and low pH conditions. Such etching first manifests itself as permanent spotting which is displeasing to the eye. After a period of time that is often dependent on temperature, there is removal or other deterioration of the coating in the spotted areas and then further deterioration in other areas and finally failure of the coating in a functional sense. Such etching takes place during the drying of droplets of water containing relatively small amounts of acidic or alkaline moieties from the substrate. As the droplet decreases in volume, the pH decreases to very low values in the case of acid moieties and increases to very high values in the case of alkaline moieties. Under these conditions, relatively rapid attack of the substrate occurs.

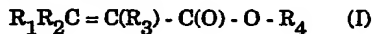


The coatings industry is actively seeking coatings with improved hydrolytic resistance particularly at high and low pH values over that of the current acrylics. Such improved resistance would result in coatings that have enhanced resistance to hostile environment as such as those caused by acid rain, by air-borne chemicals, and by cleaners used for dirt removal.

Another need in the field of coatings is low viscosity coating formulations that will allow higher application solids to be achieved and maintain or improve final cured coating performance characteristics. The requirement for such high solids coating formulations is driven by both federal and state regulations as well as a desire to decrease any impact volatile organic solvents may have on the environment. Coatings that have high solids can have an unbalanced property profile that is usually related to the low molecular weight oligomers/polymers that must be used to obtain a sufficiently low viscosity in formulated coating systems that have low volatile organic content. Coatings with high solids, low volatile organic content, and improved physical and chemical characteristics result in a decreased environmental impact caused by volatile solvents, decreased energy requirements for volatile solvent manufacture and volatilization, and a longer service life which requires less replacement and thus conserves both energy and natural resources.

#### Disclosure of the Invention

This invention relates in part to hindered-hydroxyl functional meth(acrylate) compounds represented by the formula:



wherein:

$R_1$ ,  $R_2$  and  $R_3$  are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, preferably an alkyl group of 1 to 3 carbon atoms;

$R_4$  is a substituted or unsubstituted monovalent hydrocarbon residue represented by the formula:  
 $-(CR_5R_6)_v - (CR_7R_8)_w - (C(OH)R_9)_x - (CR_{10}R_{11})_y - (CR_{12}R_{13})_z - R_{14}$

wherein:

each  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue;

$R_{14}$  is hydrogen, hydroxyl or a substituted or unsubstituted monovalent hydrocarbon residue provided  $R_{14}$  is hydroxyl when  $x$  is value of 0 and  $R_{14}$  is other than hydroxyl when  $x$  is a value of 1;

each of  $v$ ,  $w$ ,  $y$  and  $z$  is a value of from 0 to about 5 and the sum of  $v + w + x + y + z$  is a value of from about 3 to about 15; and  $x$  is a value of 0 or 1;

provided (i) at least one of  $w$  and  $y$  is a value other than 0 when  $x$  is a value of 1; (ii) at least one of  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$  and  $R_{11}$  is other than hydrogen when  $x$  is a value of 1; and (iii) at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen when  $x$  is a value of 0.

This invention also relates in part to processes for preparing hindered-hydroxyl functional (meth)acrylate compounds.

This invention further relates in part to copolymers comprising the reaction product of (a) one or more hindered-hydroxyl functional (meth)acrylate monomers and (b) at least one

other monomer copolymerizable therewith, said copolymer having (i) a number average molecular weight of less than about 12,000, preferably less than about 10,000, and most preferably less than about 7500, (ii) a glass transition temperature of from -30°C to about 100°C, preferably from about -20°C to about 65°C, and most preferably from about 0°C to about 45°C, and (iii) a styrene concentration of from 0 to less than about 20 weight percent, and said hindered-hydroxyl functional (meth)-acrylate monomer having a diacrylate content of less than about 5 weight percent.

This invention also relates in part to compositions comprising (a) the copolymer described above, (b) a crosslinking agent, and (c) optional ingredients. Such compositions include, for example, coatings, adhesives, inks, sealants and the like.

This invention further relates in part to a method of protecting a surface from corrosion when exposed to a hostile environment, e.g., an acidic or alkaline environment, which comprises applying to the surface a composition described above, and curing said composition.

#### Detailed Description

The hindered-hydroxyl functional (meth)acrylate compounds of this invention can be prepared, for example, by (i) direct esterification of appropriate diol compound with methacrylic acid or acrylic acid, (ii) reaction of appropriate diol compound with methacrylic anhydride or acrylic anhydride, and (iii) transesterification of appropriate diol compound with alkyl methacrylate or alkyl acrylate, e.g., methyl methacrylate, methyl acrylate, ethyl methacrylate, ethyl acrylate, propyl methacrylate, propyl acrylate, and the like.

The direct esterification of appropriate diol compound with methacrylic acid or acrylic acid can be conducted at a temperature of from about 100°C to 300°C for a period of about 1 hour to about 7 days with the longer time being used at the lower

temperature, preferably from about 125°C to about 200°C 1 hour to about 5 days, and more preferably at about 125°C to 150°C for about 1 hour to about 48 hours. Direct esterifications are often carried out at reflux temperature which is dependent on the boiling point temperature of the solvent used for a period of about 6 to about 8 hours. Suitable solvents include benzene, xylene, toluene and the like. One or more stabilizers such as hydroquinone, methoxyhydroquinone, phenothiazine and the like should be used to prevent polymerization.

The direct esterification reaction can be conducted over a wide range of pressures ranging from atmospheric pressure to superatmospheric pressures, e.g., from about 1 atmosphere to about 100 atmospheres or greater. It is preferable to conduct the direct esterification reaction at pressures of from about atmospheric to about 25 atmospheres. The direct esterification reaction is preferably effected in the liquid or vapor states or mixtures thereof.

The molar ratio of appropriate diol compound to methacrylic acid or acrylic acid in the direct esterification reaction is not narrowly critical and can range from about 0.05:1 or less to about 50:1 or greater, preferably from about 0.1:1 to about 10:1.

The reaction of appropriate diol compound with methacrylic anhydride or acrylic anhydride can be conducted at a temperature of from about 0°C to 150°C for a period of about 1 hour to about 7 days with the longer time being used at the lower temperature, preferably from about 15°C to about 100°C for about 1 hour to about 5 days, and more preferably at about 25°C to 50°C for about 1 hour to about 48 hours. One or more stabilizers such as hydroquinone, methoxyhydroquinone, phenothiazine, and the like should be used to prevent polymerization.

The reaction of appropriate diol compound with methacrylic anhydride or acrylic anhydride can be conducted over a wide range of pressures ranging from atmospheric pressure to superatmospheric pressures, e.g., from about 1 atmosphere to about

100 atmospheres or greater. It is preferable to conduct the reaction at pressures of from about atmospheric to about 25 atmospheres. The reaction is preferably effected in the liquid or vapor states or mixtures thereof.

The molar ratio of appropriate diol compound to methacrylic anhydride or acrylic anhydride in the reaction is not narrowly critical and can range from about 0.05:1 or less to about 50:1 or greater, preferably from about 0.1:1 to about 10:1.

The transesterification of appropriate diol compound with alkyl methacrylate or alkyl acrylate can be conducted at a temperature of from about -20°C to 250°C for a period of about 10 minutes to about 7 days with the longer time being used at the lower temperature, preferably from about 0°C to about 200°C for about 1 hour to about 5 days, and more preferably at about 0°C to 180°C for about 1 hour to about 48 hours. One or more stabilizers such as hydroquinone, methoxyhydroquinone, phenothiazine and the like should be used to prevent polymerization.

The transesterification reaction can be conducted over a wide range of pressures ranging from atmospheric pressure to superatmospheric pressures, e.g., from about 1 atmosphere to about 100 atmospheres or greater. It is preferable to conduct the transesterification reaction at pressures of from about atmospheric to about 25 atmospheres. The transesterification reaction is preferably effected in the liquid or vapor states or mixtures thereof.

The molar ratio of appropriate diol compound to alkyl methacrylate or alkyl acrylate in the transesterification reaction is not narrowly critical and can range from about 0.05:1 or less to about 50:1 or greater, preferably from about 0.1:1 to about 10:1.

Illustrative of suitable diol compounds useful in the hindered-hydroxyl functional (meth)acrylate compound preparation processes of this invention include, for example, 2-ethyl-1,3-hexanediol, 2-methyl-1,3-pentanediol, 2-propyl-1,3-heptane diol, 2-ethyl-1,3-heptane diol, 2-ethyl-1,3-propane diol, 2-i-propyl-3-i-butyl-

1,3-propane diol, 2-i-propyl-3-methyl-1,3-propane diol, 1-i-butyl-1,3-propane diol, 1-methyl-2-butyl-1,3-propane diol, 2,2,4-trimethyl-1,3-pentane diol, and the like. Preferred hindered-hydroxyl functional (meth)acrylate compounds of this invention are obtained from 2,2,4-trimethyl-1,3-pentane diol, 2-methyl-1,3-pentane diol and 2-ethyl-1,3-hexane diol. The diol compounds can be prepared by conventional methods such as aldol condensations, the reaction of formaldehyde with ketones, or other suitable methods.

Optionally the transesterification reaction mass may contain a transesterification catalyst. Illustrative of suitable transesterification catalysts are potassium bicarbonate, sodium bicarbonate, potassium thiocyanate, barium thiocyanate, calcium triocyanate, cobalt thiocyanate, sodium thiocyanate, zinc thiocyanate, other salts of weak acids such as sodium acetate, lithium acetate, calcium acetate, zinc acetate, and other metal salts of acetic acid and carbonic acid, alkali metal alkoxides such as sodium methoxide, potassium methoxide, lithium methoxide, zinc methoxide, calcium methoxide, metal oxalates, and the like. When used, the catalysts can be present in amounts of from about 0.10 mole percent or less to 20 mole percent with it preferred that from about 0.20 mole percent to about 10 mole percent be used. The transesterification catalyst may be added to the reaction mass all at one time, in discrete portions that may be of the same or different size, or in a continuous uniform or non uniform manner over the entire reaction time period or over a portion of the reaction time period.

The products produced by the processes of this invention include hindered-hydroxyl functional (meth)acrylate compounds, in particular, those hindered-hydroxyl functional (meth)acrylate compounds encompassed within Formula (I) above. These products are useful in a number of ways including imparting excellent physical characteristics, such as water resistance, chemical resistance, resistance to hostile environments such as acid rain, and

the like, to coatings, inks, adhesives, and sealants prepared from the hindered-hydroxyl functional (meth)acrylate compounds or derivatives thereof, and as reactive surfactants.

Illustrative hindered-hydroxyl functional (meth)acrylate compounds prepared by the processes of this invention include, for example, 2-ethyl-3-hydroxyhexyl methacrylate, 1-propyl-2-ethyl-3-hydroxypropyl methacrylate, 1-ethyl-2-methyl-3-hydroxypropyl methacrylate, 2-methyl-3-hydroxypentyl methacrylate, 2-propyl-3-hydroxyheptyl methacrylate, 1-butyl-2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxyheptyl methacrylate, 1-butyl-2-ethyl-3-hydroxypropyl methacrylate, 2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxypropyl methacrylate, 1-i-butyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-methyl-3-hydroxypropyl acrylate, 1-i-butyl-3-hydroxypropyl methacrylate, 3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-butyl-3-hydroxypropyl methacrylate, 2-butyl-3-hydroxybutyl methacrylate, 1-i-propyl-2,2-dimethyl-3-hydroxypropyl methacrylate, 2,2-dimethyl-3-hydroxy-4-methylpentyl methacrylate, and the like.

For purposes of Formula (I) above, the following compounds defined in (a) through (r) are outside the scope of claim 1 of this invention:

(a) when v, w and z are each a value of 1, x and y are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are each hydrogen,  $R_3$  is hydrogen or methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(b) when v and z are each a value of 1, w, x and y are each a value of 0,  $R_1$  and  $R_2$  are each hydrogen,  $R_3$  is hydrogen or methyl, one of  $R_5$  and  $R_6$  is methyl and the other is hydrogen, and

$R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(c) when  $y$  and  $z$  are each a value of 1,  $v$ ,  $w$  and  $x$  are each a value of 0,  $R_1$  and  $R_2$  are each hydrogen,  $R_3$  is hydrogen or methyl,  $R_{10}$  and  $R_{11}$  are each methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(d) when  $w$ ,  $y$  and  $z$  are each a value of 1,  $v$  and  $x$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_{10}$  and  $R_{11}$  are each hydrogen,  $R_3$  is hydrogen or methyl, one of  $R_7$  and  $R_8$  is methyl and the other is hydrogen, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(e) when  $v$ ,  $w$  and  $z$  are each a value of 1,  $y$  is a value of 2,  $x$  is a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_{10}$  and  $R_{11}$  are each hydrogen, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(f) when  $v$ ,  $w$ ,  $y$  and  $z$  are each a value of 1,  $x$  is a value of 0,  $R_1$ ,  $R_2$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_{10}$  and  $R_{11}$  are each hydrogen,  $R_3$  is methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or ethyl;

(g) when  $v$ ,  $w$  and  $z$  are each a value of 1,  $x$  and  $y$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_7$  and  $R_8$  are each hydrogen,  $R_5$  and  $R_6$  are each methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(h) when  $v$ ,  $w$ ,  $y$  and  $z$  are each a value of 1,  $x$  is a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_7$ ,  $R_8$ ,  $R_{10}$  and  $R_{11}$  are each hydrogen,



one of  $R_5$  and  $R_6$  is methyl and the other is hydrogen, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(i) when  $v$ ,  $w$  and  $z$  are each a value of 1,  $x$  and  $y$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_7$  and  $R_8$  are each hydrogen,  $R_5$  and  $R_6$  are each methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(j) when  $v$  and  $z$  are each a value of 1,  $w$ ,  $x$  and  $y$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_5$  and  $R_6$  are each hydrogen,  $R_3$  is hydrogen or methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or phenyl;

(k) when  $v$ ,  $w$  and  $z$  are each a value of 1,  $x$  and  $y$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_5$  and  $R_6$  are each hydrogen,  $R_3$ ,  $R_7$  and  $R_8$  are each methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or propyl;

(l) when  $v$ ,  $w$ ,  $x$  and  $z$  are each a value of 1,  $y$  is a value of 0,  $R_1$ ,  $R_2$ ,  $R_5$ ,  $R_6$  and  $R_9$  are each hydrogen,  $R_3$  is hydrogen or methyl, and  $R_7$  and  $R_8$  are each methyl, then at least one of  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  is other than hydrogen or methyl;

(m) when  $v$ ,  $w$ ,  $y$  and  $z$  are each a value of 1,  $x$  is a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_7$ ,  $R_8$ ,  $R_{10}$  and  $R_{11}$  are each hydrogen,  $R_5$  and  $R_6$  are each methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl;

(n) when  $v$ ,  $w$  and  $z$  are each a value of 1,  $y$  is a value of 3,  $x$  is a value of 0,  $R_1$ ,  $R_2$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_{10}$  and  $R_{11}$  are

each hydrogen,  $R_3$  is methyl, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or ethyl;

(o) when  $v$  and  $z$  are each a value of 1,  $w$ ,  $x$  and  $y$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_5$  and  $R_6$  are each hydrogen, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen, ethyl or butyl;

(p) when  $w$ ,  $x$  and  $z$  are each a value of 1,  $v$  and  $y$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_7$ ,  $R_8$  and  $R_9$  are each hydrogen, then at least one of  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  is other than hydrogen or phenyl;

(q) when  $v$  and  $z$  are each a value of 1,  $w$ ,  $x$  and  $y$  are each a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_5$  and  $R_6$  are each hydrogen, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen, methyl or phenyl; and

(r) when  $v$ ,  $w$  and  $z$  are each a value of 1,  $y$  is a value of 0,  $x$  is a value of 0,  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_{10}$  and  $R_{11}$  are each hydrogen, and  $R_{14}$  is hydroxyl, then at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen or methyl.

The hindered-hydroxyl functional (meth)acrylate compounds produced by the processes of this invention can be separated by distillation. For example, a crude reaction product can be subjected to a distillation-separation at atmospheric or reduced pressure through a packed distillation column. Reactive distillation may be useful in conducting certain reactions of this invention.

The hindered-hydroxyl functional (meth)acrylate compound preparation processes of this invention may be carried out using, for example, a fixed bed reactor, a fluid bed reactor, or a

slurry reactor. The optimum size and shape of the catalysts will depend on the type of reactor used. In general, for fluid bed reactors, a small, spherical catalyst particle is preferred for easy fluidization. With fixed bed reactors, larger catalyst particles are preferred so the back pressure within the reactor is kept reasonably low.

The hindered-hydroxyl functional (meth)acrylate compound preparation processes of this invention can be conducted in a batch or continuous fashion, with recycle of unconsumed starting materials if required. The reaction can be conducted in a single reaction zone or in a plurality of reaction zones, in series or in parallel or it may be conducted batchwise or continuously in an elongated tubular zone or series of such zones. The materials of construction employed should be inert to the starting materials during the reaction and the fabrication of the equipment should be able to withstand the reaction temperatures and pressures. Means to introduce and/or adjust the quantity of starting materials or ingredients introduced batchwise or continuously into the reaction zone during the course of the reaction can be conveniently utilized in the processes especially to maintain the desired molar ratio of the starting materials. The reaction steps may be effected by the incremental addition of one of the starting materials to the other. Also, the reaction steps can be combined by the joint addition of the starting materials. When complete conversion is not desired or not obtainable, the starting materials can be separated from the product, for example by distillation, and the starting materials then recycled back into the reaction zone.

The hindered-hydroxyl functional (meth)acrylate compound preparation processes are conducted for a period of time sufficient to produce the hindered-hydroxyl functional (meth)acrylate compounds. The exact reaction time employed is dependent, in part, upon factors such as temperature, nature and proportion of starting materials, and the like. The reaction time will normally be within the range of from about one-half to about 100

hours or more, and preferably from less than about one to about ten hours.

The hindered-hydroxyl functional (meth)acrylate compound preparation process may be conducted in either glass lined, stainless steel or similar type reaction equipment. The reaction zone may be fitted with one or more internal and/or external heat exchanger(s) in order to control undue temperature fluctuations, or to prevent any possible "runaway" reaction temperatures.

The hindered-hydroxyl functional (meth)acrylate compounds produced by the processes of this invention can undergo further reaction(s) to afford desired derivatives thereof. Such permissible derivatization reactions can be carried out in accordance with conventional procedures known in the art. Illustrative derivatization reactions include, for example, esterification, etherification, alkoxylation, amination, alkylation, hydrogenation, dehydrogenation, reduction, acylation, condensation, carboxylation, carbamoylation, oxidation, silylation and the like, including permissible combinations thereof. This invention is not intended to be limited in any manner by the permissible derivatization reactions or permissible derivatives of hindered-hydroxyl functional (meth)acrylate compounds.

More particularly, the hindered-hydroxyl functional (meth)acrylate compounds of this invention can undergo any of the known reactions of hydroxyl groups illustrative of which are reactions with acyl halides to form esters; with ammonia, a nitrile, or hydrogen cyanide to form amines; with alkyl acid sulfates to form disulfates; with carboxylic acids and acid anhydrides to form esters and polyesters; with alkali metals to form salts; with ketenes to form esters; with acid anhydrides to form carboxylic acids; with oxygen to form aldehydes and carboxylic acids; ring-opening reactions with lactones, tetrahydrofuran, and alkylene oxides such as ethylene

oxide, propylene oxide, epichlorohydrin; dehydrogenation to form aldehydes, isocyanates to form urethanes, and the like.

The hindered hydroxyl-functional (meth)acrylate compounds of the invention are useful in the formation of intermediates such as copolymers/oligomers/polymers for formulation with crosslinking agents; for preparation of alkylene oxide and lactone adducts that are useful as surfactants and/or intermediates; for preparation of urethane (meth)acrylates; for preparation of carboxyl-terminated, carbamoyl-terminated, and isocyanate-terminated (meth)acrylate adducts; and the like.

The copolymers of this invention can be prepared by conventional free-radical, chain-transfer polymerization techniques which are well known to those skilled in the art. As used herein, the term "copolymer" is contemplated to include oligomers and polymers. Chain transfer agents are compounds such as the alkyl mercaptans illustrative of which is tertiary-dodecyl mercaptan and the like; hydroxyl containing compounds such as alcohols including propanol, isopropanol, butanols, pentanol, hexanol; diols including ethylene glycol, 1,3-propane diol, 1,4-butane diol, 2,3-butane diol, pentane diols, hexane diols, and diols described herein; hydroxyl alkyl acrylates as described herein; and the like. When used, chain transfer agents are present in an amount up to about 5 percent by weight or greater based on weight of the free-radical polymerizable monomers.

Illustrative hindered-hydroxyl functional (meth)acrylate monomers useful in the copolymers of this invention include, for example, 2-ethyl-3-hydroxyhexyl methacrylate, 1-propyl-2-ethyl-3 hydroxypropyl methacrylate, 1-ethyl-2-methyl-3-hydroxypropyl methacrylate, 2-methyl-3-hydroxypentyl methacrylate, 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 2-propyl-3-hydroxyheptyl methacrylate, 1-butyl-2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxyheptyl methacrylate, 1-butyl-2-ethyl-3-hydroxypropyl methacrylate, 2-propyl-3-

hydroxypropyl methacrylate, 2-ethyl-3-hydroxypropyl methacrylate, 1-i-butyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-methyl-3-hydroxypropyl acrylate, 1-i-butyl-3-hydroxypropyl methacrylate, 3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-butyl-3-hydroxypropyl methacrylate, 2-butyl-3-hydroxybutyl methacrylate, 1-i-propyl-2,2-dimethyl-3-hydroxypropyl methacrylate, 2,2-dimethyl-3-hydroxy-4-methylpentyl methacrylate, and the like. Preferred hindered-hydroxyl functional (meth)acrylate monomers useful in this invention are obtained from 2,2,4-trimethyl-1,3-pentane diol, 2-methyl-1,3-pentane diol and 2-ethyl-1,3 hexane diol. Suitable hindered-hydroxyl functional (meth)acrylate monomers useful in preparing the copolymers of this invention include, but are not limited to, those represented by the Formula (I) above.

The hindered-hydroxyl functional (meth)acrylate monomers useful in this invention impart excellent physical characteristics, such as water resistance, chemical resistance, resistance to hostile environments such as acid rain, and the like, to coatings, inks, adhesives, and sealants prepared from the hindered-hydroxyl functional (meth)acrylate monomers or derivatives thereof.

Suitable other monomers copolymerizable with the hindered-hydroxyl functional (meth)acrylate monomers include one or more monoethylenically and/or multiethylenically unsaturated copolymerizable monomers, for example, one or more other (meth)acrylates, hydroxyalkyl (meth)acrylates, N-(alkoxymethyl)-acrylamides such as N-(iso-butoxymethyl)-acryl-amide and N-methylol-acrylamide, vinyl compounds and the like. The other copolymerizable monomer can be the same as or different from the hindered-hydroxyl functional (meth)acrylate monomer.

Illustrative of the other (meth)acrylates include, for example, acrylic acid, methacrylic acid, the esters of acrylic and methacrylic acid such as the various methyl, ethyl, propyl, butyl,

pentyl, hexyl, octyl, decyl, dodecyl, and the like acrylates including the various isomers of these and other listed compounds; bornyl, isobornyl, norbornyl and isonorbornyl acrylate; unsaturated carbamoyloxy carboxylates such as those described in U.S. Patent No. 3,674,838; 3-methacryloxypropyltris(trimethyl-siloxy)silane and 3-acryloxypropyltris(trimethyl-siloxy)silane; dicyclopentenylacrylate; hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxyhexyl acrylates, hydroxydecyl acrylates, caprolactone acrylates which are the product of reacting an  $\epsilon$ -caprolactone with a hydroxyalkyl-acrylate and which have both acrylate and hydroxyl functionality, including carbamoyloxyalkanoyloxyalkyl (meth)acrylates, ethoxylated and propoxylated acrylates which are the product of reacting an alkylene oxide illustrative of which are ethylene oxide, propylene oxide, and the like, with an hydroxyalkylacrylate; cyclohexyl acrylate, 2-phenoxyethyl acrylate, glycidyl acrylate, and the like.

Illustrative vinyl compounds include, for example, styrene, vinyl cyclohexane, vinyl cyclohexene, vinyl cyclooctane, N-vinylpyrrolidone, vinylpyridines, vinyl imidazole, vinyl naphthalene, acrylonitrile, methacrylonitrile, vinyl chloride, vinyl fluoride, vinyl bromide, vinylidene fluoride, vinylidene chloride; 5-vinyl-2-norbornene and other vinyl norbornenes; vinyl esters such as vinyl acetate, vinyl trifluoroacetate, vinyl propionates, vinyl butyrates, vinyl penanoates, vinyl 2-ethylhexanoate, vinyl nonanoates, vinyl decanoates, vinyl neonanoate, vinyl necodecanoate, vinyl neopentanoate and the like; vinyl ethers such as vinyl alcohol which is formed by the hydrolysis of vinyl acetate, vinyl acetate, vinyl propionates, vinyl triethylene glycol and the like; vinylacetic acid, 3-vinylbenzyl chloride, 4-vinylbiphenyl, vinyl carbazole, vinyl chloroformate, vinyl crotonate, vinyltrimethylsilane, vinyltrimethoxysilane, vinylferrocene, vinyltributyltin, vinyl sulfonic acid, and the like. Included within the definition of vinyl compounds is maleic anhydride, maleic acid, and maleate esters and half esters.

As indicated above, the copolymers/oligomers of this invention have (i) a number average molecular weight of less than about 12,000, preferably less than about 10,000, and most preferably less than about 7500, (ii) a glass transition temperature of from -30°C to about 100°C, preferably from about -20°C to about 65°C, and most preferably from about 0°C to about 45°C, and (iii) a styrene concentration of from 0 to less than about 20 weight percent, and the hindered-hydroxyl functional (meth)acrylate monomer has a diacrylate content of less than about 5 weight percent. These properties are important in that the compositions of this invention containing the hindered-hydroxyl functional (meth)acrylate-containing copolymers can exhibit excellent physical characteristics such as water resistance, chemical resistance, resistance to hostile environments such as acid rain and air-borne chemicals, corrosion resistance, acid etch resistance, alkaline etch resistance, low surface tension, low viscosity that will allow higher application solids to be achieved and maintain or improve final cured coating performance characteristics, and the like.

The copolymers/oligomers of this invention can be prepared by a variety of polymerization techniques illustrative of which are solution polymerization, aqueous emulsion, dispersion, or suspension polymerization, bulk polymerization, nonaqueous emulsion, dispersion, or suspension polymerization, and the like. Said polymerizations can be effected in a variety of reactors illustrative of which are stirred batch reactor, tubular reactors, and the like and can be made of various materials of construction all of which are known to those skilled in the art of conducting such polymerizations.

In a particular embodiment of this invention, the hindered-hydroxyl functional copolymers of the invention are prepared by the following process. This process is particularly useful because when the hindered-hydroxyl functional (meth)acrylate monomer described is prepared, it is difficult to



separate the starting diol from the various acrylates formed. This is because both monomeric isomers and the diol have very similar boiling points. To circumvent this difficulty, the reaction is usually carried to a high degree of completion that will minimize the amount of unreacted diol in the final reaction mass; however, this also increases the amount of undesirable diacrylate in the final product. The undesirable diacrylate must be removed by distillation so it does not cause premature crosslinking during preparation of the copolymer/oligomer of the invention. However, if the reaction of (meth)acrylic anhydride, (meth)acrylic acid, or lower alkyl(meth)acrylate is carried to only a low degree of conversion of about 50 percent or less and the excess diol is not removed before carrying out the polymerization, the amount of monoacrylate relative to diacrylate can be maximized and the final product improved. To conduct the process, appropriate diol compounds needed to form the hindered-hydroxyl functional (meth)acrylate monomers and (meth)acrylic anhydride, (meth)acrylic acid, or lower alkyl(meth)acrylate are combined in an approximately 2/1 mole ratio and allowed to react to the point at which there has been about a 50 percent by weight conversion to the appropriate mono(meth)acrylate with only small, less than about 2 percent, quantities of diacrylate formed. This point in the reaction is determined by analysis. This mixture is then combined with one or more monomers copolymerizable with the hindered-hydroxyl functional (meth)acrylate, and the polymerization to the copolymer/oligomer of the invention is carried out. After the copolymer has been prepared, it is separated from the excess diol by vacuum distillation of the diol.

In a particular embodiment of this invention, the hindered-hydroxyl functional copolymers of the invention are modified by reacting all or a portion of the hydroxyl groups pendant on the polymer with a monoisocyanate including cyanic acid and cyanogen chloride to form carbamoyloxyalkanoyloxyalkyl containing

copolymers. Included in the hydroxyl groups that can be modified are the hindered hydroxyl groups and those introduced by means of other copolymerizable ethylenically unsaturated monomers such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylates, the caprolactone acrylates all of which are mentioned above and vinyl alcohol that can be obtained by hydrolysis of vinyl acetate or other vinyl esters, and the like. To form these copolymers, the copolymers of the invention are reacted with monoisocyanates in which the reaction between the hydroxyl group and isocyanate may be represented as follows:



wherein  $\text{R}_{15}$  is hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue. It is preferred that the modification be carried out in the absence of solvents or other compounds that contain hydroxyl groups which groups would interfere with the desired isocyanate/hydroxyl reaction. If desired, said modification can be carried out on the hindered hydroxyl functional (meth)acrylate prior to copolymerization with the other ethylenically unsaturated monomers.

Suitable isocyanates are hydrogen and substituted or unsubstituted monovalent hydrocarbon monoisocyanates illustrative of which are cyanic acid, methyl isocyanate, ethyl isocyanate, propyl isocyanates, butyl isocyanates, pentyl isocyanates, hexyl isocyanates, heptyl isocyanates, octyl isocyanates, nonyl isocyanates, decyl isocyanates, and higher hydrocarbon isocyanates, chloroethyl isocyanate, chlorobutyloxypropyl isocyanate, phenyl isocyanate, o-, m-, and p- chlorophenyl isocyanates, benzyl isocyanate, naphthyl isocyanate, p-ethylphenyl isocyanate, di-chlorophenyl isocyanates, and the like. The monoisocyanates can be used alone or in admixture to modify the copolymers/oligomers of the invention.

The compositions of this invention are comprised of (a) from about 10 weight percent or less to about 90 weight percent or greater, preferably from about 40 weight percent to about 90 weight percent, of the copolymer of this invention, (b) from about 10 weight percent or less to about 90 weight percent or greater, preferably from about 10 weight percent to about 60 weight percent of a suitable crosslinking agent, and (c) optional ingredients. The compositions of this invention can be produced by conventionally formulating the hindered-hydroxyl functional (meth)acrylate-containing copolymers of this invention with one or more of a variety of crosslinking agents and optional ingredients as described below.

Illustrative crosslinking agents suitable for crosslinking the compositions of this invention include, for example, the aminoplasts, the multifunctional isocyanates, phenolics, cycloaliphatic epoxides, glycidyl epoxides; carbodiimides and polycarbodiimides, which can be used when the copolymer contains carboxylic acid or other acidic functionality; and the like. When they will not interfere with each other, mixtures of the various classes or particular crosslinking agents can be used.

To obtain maximum etch resistance, when the copolymer/oligomer containing hindered-hydroxyl functional acrylates is used said copolymer/oligomer should have an oxygen content of less than about 25 weight percent and when aminoplast crosslinking agents are used, it is preferred that said aminoplasts contain about 90% or more alkylation and when isocyanate crosslinking agents are used, it is preferred that triisocyanates are used and most preferred that triisocyanates containing some cyclic ring structure are used.

Illustrative aminoplast crosslinking agents include, for example, alkoxymelamines, melamine-formaldehydes, ureaformaldehydes, alkylated benzoguanimines, guanyl ureas, guanidines, biguanidines, polyguanidines, and the like including mixtures of these compounds. Illustrative of specific compounds are

hexamethoxymethylmelamine, methylated melamine, butylated melamine, methylated/butylated melamine, butylated urea, benzoguanidine, and the like.

Illustrative multifunctional isocyanate crosslinking agents include, for example, 4,4'-diphenylmethane diisocyanate, 4,4'-dicyclohexyl diisocyanate, 2,4- and 2,6-toluene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, meta- and para-tetramethylxylene diisocyanate, hexamethylene diisocyanate, 2,2,4- and 2,4,4- trimethylenehexamethylene diisocyanate, 4,4',4"-triisocyanato triphenylmethane, hexamethylene diisocyanate, biurets of hexamethylene diisocyanate with an average functionality greater than 2, and the like. The particular isocyanates can be used in a nascent or a blocked form with the latter type being preferred when a one-package system with maximized pot life/shelf life is desired.

The phenolic crosslinking agents useful in the practice of this invention include, for example, the soluble, heat-reactive phenols or resoles such as those described in T.S. Carswell, Phenoplasts, pages 9-29, Interscience Publishers Inc., New York (1947) and in J. A. Brydson, Plastics Materials, pages 385-386, D. Van Nostrand Co. Inc., New Jersey (1966). Illustrative of the soluble, heat-reactive phenolic crosslinking agents are monomers and polymers of alkylated phenol-formaldehyde, alkylated cresol-formaldehyde, including methylated phenol-formaldehyde, butylated phenol-formaldehyde, cresol-formaldehyde, and the like as well as the various heat reactive phenolics made by reacting phenol, propyl phenols, butyl phenols, amyl phenols, and/or higher hydrocarbon phenols, o-, m-, and p- cresol, xylenols, and the like, with formaldehyde in the presence of a suitable catalyst such as ammonia, ethylamine, triethylamine, as well as other phenols which are known in the art of making heat reactive phenolics.

Illustrative cycloaliphatic epoxide crosslinking agents include, for example, 3,4-epoxy-cyclohexylmethyl 3,4-epoxycyclo-

hexanecarboxylate, 3,4-epoxy-6-methyl-cyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate, vinyl cyclohexane diepoxide, cyclohexane diepoxide, cyclopentadiene diepoxide, limonene diepoxide, V-pinene diepoxide, 3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxycyclohexane m-dioxane, bis(3,4-epoxycyclohexylmethyl)adipate, and the like. Although polyfunctional cycloaliphatic epoxides are preferred as crosslinking agents, small amounts of up to about 25% of monoepoxides can be used in the formulation for such purposes as viscosity reduction. Illustrative of the monoepoxides are limonene monoepoxide, V-pinene monoepoxide, vinyl 3,4-epoxycyclohexane, norbornene monoepoxide, cyclohexane monoepoxide, 3,4-epoxy derivatives of alkoxyated and/or lactone derivatives of tetrahydrobenzyl alcohol, and the like.

Illustrative of the glycidyl epoxide crosslinking agents are the diglycidyl ether of bisphenol A, higher homologs of the diglycidyl ether of bisphenol A, diglycidyl ethers of brominated bisphenol A, 1,4-butanediol diepoxide, epoxy esters, epoxy silanes, epoxy siloxanes, epoxy novolacs, and the like.

In an embodiment of this invention, a copolymer containing an N-(alkoxymethyl)acrylamide such as N-(isobutoxymethyl)acrylamide is used as a crosslinking agent for the hindered-hydroxyl functional (meth)acrylate-containing copolymers of this invention. Thus, a copolymer can be prepared from (a) an N-(alkoxymethyl)acrylamide and (b) one or more monomers copolymerizable therewith. This copolymer can be combined with any of the copolymers of this invention and optionally an acidic catalyst to prepare coating compositions as described herein.

The formulated, uncured compositions containing the copolymers of the invention and cycloaliphatic epoxides can be cured with ultraviolet light when suitable photoinitiators are included in the formulation. The photoinitiators that can be used are of the onium salt type. The ratio of copolymer to cycloaliphatic epoxide can vary broadly in the photocurable compositions, since a wide variety of

hard or soft coatings can be made. However, it is preferred that from about 1 to about 50 parts of the copolymer and from about 50 to 99 parts of the cycloaliphatic epoxide be used in the compositions, and more preferred from about 1 to about 30 parts of the copolymer and from about 70 to about 99 parts of the cycloaliphatic epoxide be used. If desired, polyols can be added to the formulation as well as surfactants and acrylates, particularly multifunctional acrylates. Illustrative of the polyols that can be used include poly-ε-caprolactone polyols, polyester polyols, polyoxypropylene polyols, poly(oxypropylene/oxyethylene) polyols, polyoxyethylene polyols, polycarbonate polyols, poly(tetramethylene oxide) polyols, ethylene glycol, 1,4-butanediol, 2-ethyl-3-propyl-1,5-pentanediol, 1,6-hexanediol, and the like. Illustrative of the acrylates that can be used include 2-ethyl hexyl acrylate, trimethylol-propane triacrylate, 1,6-hexanediol diacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, higher functional acrylates, and the like.

Illustrative of the onium salt photoinitiators useful in the photocurable coating compositions of this invention containing mixtures of the copolymers of the invention, cycloaliphatic epoxides, and optional ingredients one can mention one or more of a metal fluoroborate and a complex of boron trifluoride as described in U.S. Patent No. 3,379,653; a bis(perfluoroalkylsulfonyl)methane metal salt, as described in U.S. Patent No. 3,586,616; an aryl diazonium compound as described in U.S. Patent No. 3,708,296; an aromatic onium salt of Group VIa elements as described in U.S. Patent No. 4,058,400; an aromatic onium salt of Group Va elements as described in U.S. Patent No. 4,069,055; a dicarbonyl chelate of a Group IIIa-Va element as described in U.S. Patent No. 4,068,091; a thiopyrylium salt as described in U.S. Patent No. 4,139,655; a Group VIb element in an  $MF_6$  anion where M is selected from phosphorous, antimony, and arsenic as described in U.S. Patent No. 4,161,478; an arylsulfonium complex salt as described in U.S. Patent No.

4,231,951; an aromatic iodonium complex salt and an aromatic sulfonium complex salt, as described in U.S. Patent 4,256,828; and a bis(4-diphenylsulfonio)phenyl sulfide-bis-hexafluorometallic salts such as the phosphate, arsenate, antimonate and the like as described by W. R. Watt and coworkers in J. Polymer Sci.: Polymer Chem. Ed., 22, 1789 (1984). Preferred cationic photoinitiators include the arylsulfonium or arylodonium complex salts, aromatic sulfonium or iodonium salts of halogen containing complex ions, and aromatic onium salts of Group II, V, and VI elements. Some of such salts are commercially available in a solution form as FX-512, thought to be an arylsulfonium hexafluorophosphate, from 3M Company, CYRACURE UVR-6990 and UVR-6974, arylsulfonium hexafluorophosphate and arylsulfonium hexafluoroantimonate, respectively, from Union Carbide Chemicals and Plastics Company Inc.; UVE-1014 and UVE-1016, arylsulfonium hexafluorophosphate and arylsulfonium hexafluoroantimonate, respectively, from General Electric Company, KI-85, thought to be bis(4-(diphenylsulfonio)phenyl)sulfide-bis-hexafluorophosphate, from Degussa AG; and SP-150 and SP-170, thought to be bis(4-(diphenylsulfonio)phenyl)sulfide-bis-hexafluoro-phosphate and bis(4-(diphenylsulfonio)phenyl)sulfide-bis-hexafluoroantimonate, respectively, from Asahi Denka Kogyo K.K. The onium salt photoinitiators are used at a concentration of less than about 0.1 weight percent to about 10 weight percent, preferably at concentrations of about 0.3 weight percent to about 5 weight percent of the total composition.

It is preferable that a catalyst be used for curing or crosslinking of certain of the compositions of this invention. Illustrative catalysts for thermal curing of the coating compositions when aminoplasts and cycloaliphatic epoxides are used include, among others, p-toluene sulfonic acid and its salts such as ammonium p-toluene sulfonate, diethylammonium sulfonate, diisopropylammonium p-toluene sulfonate, and the like;

dodecylbenzene sulfonic acid and its salts such as ammonium dodecylbenzene sulfonate, diethylammonium dodecylbenzene sulfonate, and the like; phosphoric acid and its salts; dinonylnaphthalene sulfonic acids and their salts such as ammonium dinonylnaphthalene sulfonic acids, dipropylammonium dinonylnaphthalene sulfonic acids; diethylammonium dinonylnaphthalene sulfonic acids, and the like; boron trifluoride etherate; trimellitic acid; triflic acid and its salts such as diethylammonium triflate, ammonium triflate, diisopropylammonium triflate, and the like; and when isocyanates are used include, among others, zinc octanoate, stannous octanoate, dibutyltin dilaurate, amines, and the like. The triflic acid salts are particularly useful when cycloaliphatic epoxides are used as the crosslinking agents since they afford low temperature curing conditions to be used along with very good shelf stability at high solids. These catalysts are used in amounts of from about 0.02 weight percent to about 4 weight percent, preferably from about 0.05 weight percent to about 1.0 weight percent, and most preferably from about 0.1 weight percent to about 0.8 weight percent.

The compositions of this invention can be formulated to contain a variety of additives including antioxidants, ultraviolet light stabilizers; surfactants or other flow and leveling agents illustrative of which are silicone oils, acrylic polymers such as the Modaflow® Polymers available from Monsanto Company, silicone/alkylene oxides, fluorocarbon surfactants, and the like; fillers, pigments, colorants, thickeners; reactive diluents; one or more inert solvents illustrative of which are toluene, pentyl propionate, 1,1,1-trichloroethane, ethoxyethyl acetate, propoxyethyl acetate, ethoxybutyl acetate, butyl acetate, methyl isobutyl ketone, mineral spirits, methyl ethyl ketone, methyl amyl ketone, xylene, and the like; inert polymers, waxes, adhesion promoters; slip agents illustrative of which are the silicone oils, powdered polytetrafluoroethylene and/or polyethylene and the like. The



additives can be employed in conventional amounts known in the art.

The coating compositions of this invention can be applied and cured on a variety of substrates known to those skilled in the art of coatings technology. Illustrative of such substrates are steel, treated steel, tin-plated steel, galvanized steel, treated and untreated aluminum, glass, wood, paper, coated or printed paper, epoxy/fiberglass composites, polymers such as poly(ethylene terephthalate), poly(butylene terephthalate), treated polyethylene and polypropylene, vinyl film, vacuum or vapor deposited aluminum, gold, copper, silver, zinc, nickel, tin, and other metals, electroless nickel, copper-nickel alloys and the like, electrodeposited metals such as silver, copper, nickel, chromium, silver-copper alloys, and the like, glass-reinforced unsaturated-polyester/styrene products, and the like. Illustrative application methods include, for example, spraying, brushing, dipping, roll coating or other methods.

As indicated above, the compositions of this invention are useful as coatings, adhesives, inks, sealants and the like. The coating compositions of this invention include, for example, water-borne coatings, solvent-borne coatings, powdered coatings, colored coatings, clear coatings, and the like. The coating compositions of this invention are useful in a variety of applications including industrial, architectural, automotive, outdoor signs, outdoor furniture, appliance coatings, recreational vehicles, boats and the like. A particular attribute of the coating compositions of this invention is their durability in outdoor weathering, i.e., providing protection to substrates from various forms of corrosion and deterioration in a functional sense.

For purposes of this invention, the term "hydrocarbon" is contemplated to include all permissible compounds having at least one hydrogen and one carbon atom. In a broad aspect, the permissible hydrocarbons include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and

nonaromatic organic compounds which can be substituted or unsubstituted.

As used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds unless otherwise indicated. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of organic compounds. Illustrative substituents include, for example, alkyl, alkyloxy, aryl, aryloxy, hydroxy, hydroxyalkyl, amino, aminoalkyl, halogen and the like in which the number of carbons can range from 1 to about 20 or more, preferably from 1 to about 12. The permissible substituents can be one or more and the same or different for appropriate organic compounds. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

As used herein, the molecular weights were determined by gel permeation chromatography using polystyrene calibration standards.

Certain of the following examples are provided to further illustrate this invention.

#### Glossary of Terms

Aminoplast 1 - A hexamethoxymelamine commercially available from American Cyanamid as Cymel® 303.

Aminoplast 2 - A methylated/butylated melamine commercially available from Monsanto Company as Resimene® 755.

Blocked Isocyanate 1 - A blocked isocyanate, that is thought to be a methyl ethyl ketone oxime blocked trimer of 4,4'-dicyclohexanemethyl diisocyanate, commercially available from Miles, Inc. under the designation Desmodur BL-3174A.

Catalyst 1 - A 40% by weight solution of para-toluene sulfonic acid in methanol.

Catalyst 2 - Dibutyltin dilaurate.

Surfactant 1 - A 25% by weight solution in methyl amyl ketone of a silicone-based surfactant commercially available from Union Carbide Chemicals and Plastics Company Inc. as Silwet® L-7001.

Surfactant 2 - A 25% by weight solution in methyl amyl ketone of a silicone-based surfactant commercially available from Union Carbide Chemicals and Plastics Company Inc. as Silwet® L-77.

Photoinitiator 1 - An aryl sulfonium hexafluoroantimonate photoinitiator that is commercially available from Union Carbide Chemicals and Plastics Company Inc. as Cyracure® UVI-6974.

Double Rubs - Solvent resistance was measured as the number of solvent (methyl ethyl ketone double rubs or acetone double rubs) that were required to cut through the coating. If 100 rubs or more did not cut through the coating, the coating was recorded as >100. To perform the test, the solvent-soaked cloth was rubbed back and forth with hand pressure. A rub back and forth was designated as one "double rub."

Crosshatch Adhesion - Procedure conducted in accordance with ASTM D 3359-87.

Pencil Hardness - Procedure conducted in accordance with ASTM D 3363-74.

60° Gloss - Procedure conducted in accordance with ASTM D 523.

20° Gloss - Procedure conducted in accordance with ASTM D 523.

Impact Resistance. Procedure conducted in accordance with ASTM D 2794-84.

Acid etch resistance - A Fini automatic transfer pipette was used to place a series of 50 micro-liter droplets of sulfuric acid solution at approximately 1/4-inch intervals in two rows along the length of one or more coated panels. Usually two panels were required to provide the length of surface needed to examine the temperature range of 40° to 100°C that were achieved in the gradient temperature oven. Two rows of spots were used for duplication of the test. The coated panels were placed in an end-to-end position on the heating bank of a BYK Chemie gradient temperature oven and the first spots were aligned with the #1 rod which was a 40°C which resulted in the various spots being at temperatures that ranged to 100°C. The sulfuric acid solution droplets, which were of indicated acidity, were allowed to contact the coating for various times at the indicated temperatures. After the desired heating time, the panels were removed from the gradient oven, cooled to room temperature, rinsed thoroughly with distilled water, lightly patted dry, and evaluated.

Evaluation was accomplished by examining the areas that had been covered with the droplets with a 10-power, lighted magnifier. The following points of comparison were observed and recorded for each coating.

a) The lowest temperature spot area with a visible defect in the coating. A "visible defect" is the first sign of any blush, bubbling, yellowing, or other visible change.

b) The lowest temperature spot with a severe defect. A "severe defect" is blistering or complete removal of the coating with the substrate visible. This latter factor means the acidic solution has cut through the coating to the substrate.

c) A scaled 1 to 5 rating of any defect or change occurring specifically in the 50°C, 60°C, and 70°C areas of the coating using the following rating system.

1 - Fail. Coating is cut to the substrate or has severe bubbling.

- 2 - Severe. Small blister or bubble present in the coating.
- 3 - Moderate. Pinhole defect or slight change in surface of coating by fingertip feeling or visible loss of gloss.
- 4 - Slight. Blushing or yellowing of coating with no change by fingertip feeling.
- 5 - Unchanged. No visible evidence of any effect.

#### Examples

Preparation A. A methacrylate ester of 2,2,4-trimethyl-1,3-pentanediol was prepared by placing 1800 grams (12.33 moles) of 2,2,4-trimethyl-1,3-pentanediol (TMPD) in a four-neck, glass reaction flask equipped with a Therm-O-Watch temperature control device, a nitrogen inlet and outlet, a stirrer, and a feeding port. The TMPD was melted and dried by heating to 85°C while flowing dry nitrogen through the reactor for 2 hours. Then 4.0 grams of methoxyhydroquinone, 4.0 gram of phenothiazine, and 2,277 grams (14.79 moles) of freshly distilled methacrylic anhydride were added. While stirring and employing a nitrogen purge, 81.0 grams of distilled pyridine were added and the reaction mass was heated to and held at 35°C for 1-2 days after which time gas chromatographic analysis indicated that the reaction was complete. Excess methacrylic anhydride was quenched by first adding methanol, and these reaction products as well as methacrylic acid formed during the desired alkylmethacrylate ester formation were removed by washing with water. Gas chromatography, mass spectrometry, and Fourier-transform infrared analyses indicated that both monomethacrylate isomers and the expected diacrylate had formed. The monomethacrylates were separated from the diacrylate by fractional distillation.

Example 1 and Control Examples A and B. Example 1 copolymer/oligomer was prepared from a 300-gram mixture of the Preparation A alkyl monomethacrylate mixture, butyl acrylate, and methyl methacrylate. For comparison purposes, mixtures

containing hydroxyethyl methacrylate (Control A) or hydroxypropyl methacrylate (Control B) were used in the same molar amount as the Preparation A methacrylate of Example 1 and approximately equal amounts of butyl acrylate and methyl methacrylate so the total amount of monomer mixture equaled about 300 grams. A chain transfer agent, 3-mercapto-1-propanol, was included in the monomer mixture. The initial pentyl propionate solvent was placed in a 2-liter, four-neck, glass reaction flask equipped with a mechanical stirrer, a Thermo-watch heat controller, a nitrogen sparger, a water-cooled condenser, and 500-milliliter and 125-milliliter addition funnels. A nitrogen sparge was maintained throughout the procedure. The solvent was heated to 125°C, and the monomer mixture was fed by means of a piston pump to the flask over a four-hour period while controlling the temperature at 125°C. Concurrently, the initiator mixture consisting of t-amyl peroxyacetate (Lupersol 555M60) initiator dissolved in pentyl propionate was fed to the reaction flask via a second piston pump over the same time period. The two feeds were introduced into the reactor below the liquid surface and from opposite sides of the reactor. After completion of the feeding step, the monomer line was flushed with pentyl propionate and the reaction was allowed to proceed for 30 minutes at 125°C. Then a second initiator feed consisting of a mixture of t-amyl peroxyacetate dissolved in pentyl propionate was fed to the reaction mass and the reaction was allowed to proceed for an additional 2 hours at 125°C. The solution of copolymer was then cooled to room temperature and analyzed by gel permeation chromatography using polystyrene standards to determine relative average molecular weights, for total solids content, and for viscosity. The results indicated that Example 1 copolymer/oligomer prepared from Preparation A hydroxyalkyl methacrylate had a lower molecular weight and lower viscosity (Brookfield viscosity), characteristics which allow preparation of

higher total solids coating formulations, than Control Examples A and B copolymers/oligomers.

	Example	Control Examples	
	1	A	B
Initial pentyl propionate solvent, g	100.0	100.0	100.0
<b>Monomer Mixture, g(mol)</b>			
Preparation A hydroxy-alkyl methacrylate	120.0(0.56)	—	—
Hydroxyethyl methacrylate	—	72.9(0.56)	—
Hydroxypropyl methacrylate	—	—	80.7(0.56)
Butyl acrylate	90.0(0.62)	113.1(0.78)	109.5(0.75)
Methyl methacrylate	90.0(0.90)	114.0(1.14)	108.5(1.09)
3-Mercapto-1-propanol	1.80	1.80	1.80
<b>Initiator Mixture, g</b>			
Pentyl propionate	62.7	62.7	62.7
t-Amylperoxyacetate	18.3	18.3	18.3
<b>Monomer Line Flush</b>			
Pentyl propionate, g	15.0	15.0	15.0
<b>Second Initiator Mixture, g</b>			
Pentyl propionate	15.0	15.0	15.0
t-Amylperoxyacetate	1.7	1.7	1.7
<b>Copolymer Properties</b>			
Total Solids, %	58.92	58.41	59.38
$M_n$	2,383	2,778	3,191
$M_w$	6,306	9,569	8,215
$M_w/M_n$	2.64	3.44	2.57
Viscosity, cP(°C)	630(20°C)	1,130(21°C)	1,190(21°C)



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Example 2 and Control Example C. The copolymer/oligomer of Example 1 and that of Control Example A were formulated into thermally-curable coating systems by weighing the ingredients identified below into glass containers, stirring well, and applying to 4-inch x 6-inch Bonderite-952 steel panels using a 10-mil (254-micron) wet-clearance applicator. The coated panels were thermally cured in a 140°C circulating-air oven for 30 minutes. Several panels of each coating system were prepared in this manner. The results indicated that the coating of Example 2 had improved hardness, crosshatch adhesion, and acid etch resistance at pH 3.0 in comparison to the coating of Control Example C.

	<u>Example 2</u>	<u>Control</u> <u>Example C</u>
<u>Ingredients, grams</u>		
Example 1 oligomer	10.0	---
Control Example A oligomer	---	10.0
Aminoplast 1	2.0	2.0
Surfactant 1	0.16	0.16
Surfactant 2	0.16	0.16
Methyl amyl ketone solvent	1.0	1.0
Catalyst 1	0.05	0.05
<u>Cured Coating Properties</u>		
Film Thickness	2.3	2.3
Double rubs	>100	>100
60° Gloss	95.3	95.8
20° Gloss	83.9	82.4
Pencil hardness	3H	2H
Crosshatch adhesion	5B	4B
Impact resistance, in.lbs., forward/reverse	40/2	40/2
<u>Acid etch resistance</u>		
pH 2.0, 30 minutes,		
at 50°C	4/4	3/3
at 60°C	3/3	1/1
Temperature first visible defect, °C	48/48	40/40
Temperature first severe defect, °C	68/68	7/60
Water spot test	5/5	5/5

Example 3 and Control Example D. The copolymer/oligomer of Example 1 and that of Control Example A were formulated into thermally-curable coating systems and applied in a similar manner as in Example 2 and Control Example C except different amounts of catalyst and aminoplast were used. The coated panels were thermally cured at different (lower) temperatures than were used for Example 2 and Control Example C to determine the effect of cure temperature on properties. Cure time was 30 minutes. Several panels of each coating system were prepared in this manner. The results indicated that the coating of Example 3 had equivalent solvent resistance, equivalent or better hardness, and markedly improved acid-etch resistance than the coating of Control Example D.

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	<u>Example 3</u>		<u>Control Example D</u>	
<u>Ingredients, grams</u>				
Example 1 oligomer	10.0		---	
Control Example A oligomer	---		10.0	
Aminoplast 1	1.90		1.95	
Surfactant 1	0.16		0.16	
Surfactant 2	0.16		0.16	
Methyl amyl ketone solvent	1.0		1.0	
Catalyst 1	0.31		0.31	
<u>Cured Coating Properties</u>	<u>Example 3</u>		<u>Control Example D</u>	
Cure temperature, °C	110	125	110	125
Double rubs	>100	>100	>100	>100
Pencil hardness	F	H	F	F
<u>Acid etch resistance</u>				
pH = 2.0, 30 minutes				
contact at 50°C	3/3	3/3	3/3	2/2
at 60°C	1/2	2/2	1/2	1/1
Temperature first visible defect, °C	47/47	50/50	45/48	49/49
Temperature first severe defect, °C	60/62	5/65	60/62	3/53
10% acid, 15 minutes contact				
at 50°C	5/5	5/5	5/5	5/5
at 60°C	4/4	5/5	1/1	1/1
Temperature first noticeable defect, °C	58/58	65/67	56/58	53/53
Temperature first severe defect, °C	62/64	70/70	60/60	60/60

Example 4 and Control Example E. The copolymer/oligomer of Example 1 and that of Control Example A were formulated into thermally-curable, isocyanate crosslinked coating systems by weighing the ingredients identified below into glass containers, stirring well, and applying to 4-inch x 6-inch Bonderite-952 steel panels using a 10-mil (254-micron) wet-clearance applicator. The coated panels were thermally cured in a 140°C circulating-air oven for 45 minutes. Several panels of each coating system were prepared in this manner. The results indicated that the coating of Example 4 had improved adhesion, 60° gloss, 20° gloss and improved or equivalent acid etch resistance at pH 2.0 than the coating of Control Example E.

	<u>Example 4</u>	<u>Control Example E</u>
<u>Ingredients, grams</u>		
Example 1 oligomer	10.0	---
Control Example A oligomer	----	10.0
Blocked Isocyanate 1	5.0	5.0
Surfactant 1	0.20	0.20
Catalyst 2	0.20	0.20
Methyl amyl ketone, solvent	2.0	2.0
<u>Cured Coating Properties</u>		
Film Thickness	1.7	1.6
Double rubs	>100	>100
60° Gloss	97.6	82.7
20° Gloss	75.8	55.6
Pencil hardness	F	F-H
Crosshatch adhesion	5B	4B
Impact resistance, in.lbs., forward/reverse	160/70	160/120
<u>Acid etch resistance</u>		
pH = 2.0, 30 minutes contact		
at 50°C	4/4	4/4
at 60°C	3/3	2/3
Temperature first visible defect, °C	53/54	50/50
Temperature first severe defect, °C	64/65	64/64

Example 5. In a similar manner as described in Example 1, a copolymer/oligomer of higher viscosity was prepared by reacting 110.8 grams (0.52 moles) of Preparation A hydroxyalkyl methacrylate, 35.6 grams (0.25 moles) of butyl acrylate, and 53.6 grams (0.54 moles) of methyl methacrylate in 100 grams of pentyl propionate (solvent) and in the presence of 0.14 grams of 3-mercapto-1-propanol chain-transfer agent. The initiator feed was 6.7 grams of t-amyl peroxyacetate catalyst in 63.3 grams of solvent, the post initiator feed was 0.5 grams of chain transfer catalyst in 15 grams of solvent, and the monomer-line flush was 15 grams of solvent.

The resulting oligomer/polymer had a number average molecular weight of 2,991, a weight average molecular weight of 8,334, a polydispersity of 2.79, and a viscosity of 2,090 centipoise.

Example 6. In a similar manner as described in Example 5, a copolymer/oligomer was prepared by reacting 60.0 grams of styrene, 120.0 grams of Preparation A hydroxyalkyl methacrylate, 120.0 grams of 2-ethylhexyl methacrylate, 6.0 grams of methacrylic acid, and 1.80 grams of 3-mercapto-1-propanol in 95 grams of pentyl propionate (solvent). The initiator feed was 10 grams of t-amyl peroxyacetate catalyst in 70 grams of solvent, the post initiator feed was 0.9 grams of chain transfer catalyst in 15 grams of solvent, and the monomer-line flush was 15 grams of solvent.

The resulting oligomer/polymer had a number average molecular weight of 5,557, a weight average molecular weight of 11,342, a polydispersity of 2.04, and a viscosity of 738 centipoise.

Example 7 and Control Example F. Example 7 copolymer/oligomer was prepared from a 300-grams of a mixture of the Preparation A alkyl monomethacrylate mixture, vinyl pivalate, and vinyl 2-ethylhexanoate in the amounts described below. For comparison purposes, Control Example F was prepared from a mixture containing hydroxyethyl methacrylate, vinyl pivalate, and vinyl 2-ethylhexanoate. The copolymers were prepared in a similar

manner as described in Example 1 except the quantities of materials indicated below were used, and the initiator was t-butyl peroxybenzoate. The results indicated that Example 7 copolymer prepared from Preparation A hydroxyalkyl methacrylate had a lower molecular weight and viscosity than that of Control Example F, properties which allow preparation of higher total solids coating formulations. The total solids of Control Example F oligomer were about 2% higher than those of Example 7 oligomer, which would have an effect on the measured viscosity difference.



	<u>Example 7</u>	<u>Control Example F</u>
Initial pentyl propionate solvent, g	100.0	100.0
<u>Monomer Mixture, g</u>		
Preparation A hydroxy-alkyl methacrylate	60.0	---
Hydroxyethyl methacrylate---		60.0
Vinyl privalate	180.0	180.0
Vinyl 2-ethylhexanoate	60.0	60.0
3-Mercapto-1-propanol	0.29	1.74
<u>Initiator Mixture, g</u>		
Pentyl propionate	70.0	70.0
t-Butylperoxybenzoate	11.0	11.0
<u>Monomer Line Flush</u>		
Pentyl propionate, g	15.0	15.0
<u>Second Initiator Mixture, g</u>		
Pentyl propionate	15.0	15.0
t-Butylperoxybenzoate	1.0	1.0
<u>Copolymer Properties</u>		
Total Solids, %	60.84	62.66
$M_n$	1,802	2,114
$M_w$	4,892	5,027
$M_w/M_n$	2.71	2.38
Viscosity, cP	183	260

Examples 8, 9 and 10 and Control Examples G and H. The copolymer/oligomer of Example 7 and that of Control Example F were formulated into thermally-curable, aminoplast crosslinked coating systems by weighing the ingredients described below into glass containers, stirring well, and applying to 4-inch x 6-inch Bonderite-952 steel panels using a 10-mil (254-micron) wet-clearance applicator. Before using for formulation, the Control Example F oligomer was concentrated to a total solids of 79.3% by weight by removal of pentyl propionate solvent. The coated panels were thermally cured in a 140°C circulating-air oven for 30 minutes. Several panels of each coating system were prepared in this manner.

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<u>Examples and Control Examples</u>					
	<u>R</u>	<u>G</u>	<u>S</u>	<u>10</u>	<u>H</u>
<u>Ingredients, grams</u>					
Example 9 oligomer	10.0	---	10.0	10.0	----
Control Example H oligomer	---	10.0	---	---	10.0
Aminoplast 1	0.60	2.07	---	---	----
Aminoplast 2	----	---	1.41	2.0	2.0
Surfactant 1	0.13	0.20	0.16	0.16	0.16
Surfactant 2	0.14	0.20	0.16	0.16	0.16
Catalyst 1	0.14	0.32	0.05	0.05	0.05
Methyl amyl ketone, solvent	---	2.5	---	---	----
Oligomer hydroxyl to aminoplast alkyloxy molar ratio	1/2.74	1/2.74	1/2.74	1/3.97	1/2.4
<u>Cured Coating Properties</u>					
Film Thickness	2.5	2.3	2.2	2.5	2.1
Double rubs	100	>100	>100	>100	>100
60° Gloss	86.7	96.4	96.2	97.1	93.9
20° Gloss	74.1	84.6	79.4	84.9	79.7
Pencil hardness	2B	H	HB	F	F
Crosshatch adhesion	1B	4B	5B	5B	4B-5B
Impact resistance in lbs., forward/reverse	4/2	40/2	30/2	40/2	40/2
<u>Acid etch resistance</u>					
pH = 2.0, 30 minutes contact					
at 50°C	4/4	3/3	5/5	3/3	1/1 <sup>+</sup>
at 60°C	2/1	/1	3/3	1/1	1/1
Temperature first visible defect, °C	45/47	45/48	52/52	50/50	50/50
Temperature first severe defect, °C	62/60	60/60	66/66	58/60	50/50
10% acid, 15 minutes contact					
at 50°C	5/5	5/5	5/5	5/5	5/5
at 60°C	4/4	1/1 <sup>+</sup>	4/4	5/5	4/4
Temperature first visible defect, °C	60/60	55/55	60/62	62/64	62/62
Temperature first severe defect, °C	64/64	58/58	70/70	70/70	65/65

<sup>+</sup> Coating was cut through to bare steel, i.e., very severe attack.

Example 11. A 4-necked glass reactor is equipped with a stirrer, temperature-measuring device, gas sparge, condenser, and a feeding port. Two moles (228 grams) of  $\epsilon$ -caprolactone are added to the reactor and heated to and held at 100°C for 30 minutes while sparging with dry nitrogen. The temperature is then increased to 130°C and the sparge is changed to dry air. Then, one mole (214 grams) of the Preparation A methacrylate ester is added along with 500 parts per million of the monomethylether of hydroquinone and 50 parts per million of stannous octanoate. The reaction mass is held at 130-135°C for 6 hours after which time it is cooled to room temperature. This caprolactone acrylate is stored for future use.

Example 12. One hundred grams (0.226 moles or equivalents) of the caprolactone acrylate of Example 11 is placed in the Example 11 reactor and heated to 45°C while maintaining an air sparge. Then 29.6 grams (0.113 moles or 0.226 equivalents) of 4,4'-dicyclohexylmethyl diisocyanate are added. A small exotherm is noted. The reaction is allowed to proceed at 45°C-50°C for 10 hours after which time the urethane acrylate reaction product is cooled to room temperature and stored with an air blanket for later use in radiation-cure formulations.

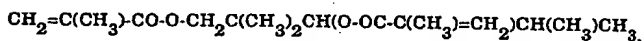
Example 13. One hundred grams (0.467 moles or equivalents) of the Preparation A methacrylate ester are placed in the Example 11 reactor. The acrylate ester is heated to 45°C while maintaining an air sparge. Then 61.2 grams (0.234 moles or 0.467 equivalents) of 4,4'-dicyclohexylmethyl diisocyanate are added. A small exotherm is noted. The reaction is allowed to proceed at 45°C-50°C for 10 hours after which time the urethane acrylate reaction product is cooled to room temperature and stored with an air blanket for later use in radiation-cure formulations.

Example 14. To an amber-colored glass container, 20 grams of the acrylic oligomer of Example 1, 40 grams of 3,4-epoxycyclohexyl 3,4-epoxycyclohexane carboxylate, and 1.8 grams of

Photoinitiator 1 are added. The ingredients are well mixed and then applied to a steel panel by the draw-down method. The coated panel is then placed on a conveyor moving at 30 feet/minute and passing under a 300 watt-per-inch medium-pressure mercury vapor lamp to effect cure. A tack-free, clear coating results.

Example 15. Ten grams of the acrylate oligomer of Example 5, 30 grams of 3,4-epoxycyclohexyl 3,4-epoxycyclohexane carboxylate, 1.5 grams of diethylammonium triflate catalyst, and 5 grams of methyl amyl ketone solvent are added to a glass container and well mixed. The mixture is coated onto a steel panel with a No. 22 wire-wound rod. The coated panel is allowed to air dry for 10 minutes and then it is oven baked at 115°C for 20 minutes. A clear, tack-free coating with good water resistance results.

Example 16. In a similar manner as described in Example 5, a copolymer/oligomer was prepared by placing 100 grams of pentyl propionate in the reactor and adding 100.50 grams of isodecyl methacrylate, 115 grams of the Preparation A hydroxyalkyl acrylate, about 5 grams of a diacrylate with the following structure,



73.50 grams of isobornyl methacrylate, 6 grams of methacrylic acid, and 0.21 grams of 3-mercapto-1-propanol. The initiator feed was composed of 10 grams of t-amyl peroxyacetate dissolved in 70 grams of pentyl propionate, the post initiator feed was composed of 0.9 grams of t-amyl peroxyacetate dissolved in 15 grams of pentyl propionate, and the monomer line flush was 15 grams of pentyl propionate. The resulting polymer had a Brookfield viscosity of 715 cP at a total solids content of 54.58%, which indicated it would be useful for preparing high solids coatings.

Examples 17 and 18. These copolymers were prepared from a 300-gram mixture of a Preparation A alkyl monomethacrylate mixture, and other copolymerizable ethylenically

unsaturated monomers as indicated below. The initial butyl propionate solvent was placed in a 2-liter, four-neck, glass reaction flask equipped with a mechanical stirrer, a Thermo-watch heat controller, a nitrogen sparger, a water-cooled condenser, and 500-milliliter and 125-milliliter addition funnels. A nitrogen sparge was maintained throughout the procedure. The solvent was heated to 140°C, and the monomer mixture was fed by means of a piston pump to the flask over a four-hour period while controlling the temperature at 140°C. Concurrently, the initiator mixture consisting of t-amyl peroxyacetate initiator dissolved in butyl propionate was fed to the reaction flask by a second piston pump over the same time period. The two feeds were introduced into the reactor below the liquid surface and from opposite sides of the reactor. After completion of the feeding step, the monomer line was flushed with 15g butyl propionate and the reaction was allowed to proceed for 30 minutes at 140°C. Then a second initiator feed consisting of a mixture of 2,5-dimethyl-2,5-di(2-ethylhexanoyl-peroxy)hexane dissolved in butyl propionate was fed to the reaction mass and the reaction was allowed to proceed for an additional 2 hours at 140°C. The solution of copolymer was then cooled to room temperature and analyzed by gel permeation chromatography using polystyrene standards to determine relative average molecular weights, for total solids content, and for viscosity. In each case, low viscosity products that were useful in coating formulations were prepared.

	<u>Examples</u>	
	<u>17</u>	<u>18</u>
Initial butyl propionate solvent, g	100.0	100.0
<u>Monomer Mixture, g(mol)</u>		
Preparation A hydroxy-alkylmethacrylate	120.0	120.0
Lauryl methacrylate	105.0	105.0
t-Butyl methacrylate	69.0	---
Methyl methacrylate	---	69.0
Methacrylic acid	6.0	6.0
<u>Initiator Mixture, g</u>		
Butyl propionate	70.0	70.0
t-Amylperoxyacetate*	10.0	10.0
<u>Monomer Line Flush</u>		
Pentyl propionate, g	15.0	15.0
<u>Second Initiator Mixture, g</u>		
Pentyl propionate	15.0	15.0
2,5-Dimethyl-2,5-di(2-ethyl hexanoylperoxy)hexane**	0.9	0.9
<u>Copolymer Properties</u>		
Total Solids, %	55.1	56.7
M <sub>n</sub>	4528	5397
M <sub>w</sub>	9285	10,620
M <sub>w</sub> /M <sub>n</sub>	2.05	1.97
<u>Viscosity<sup>+</sup>, cP, 25°C</u>	299	717

\* Lupersol 555M60(60TS)

\*\*Lupersol 256

+ Brookfield viscosity

Example 19. The copolymer of Example 18 is reacted with butyl isocyanate using 75% of the moles of butyl isocyanate required for reaction with the available hydroxyl groups on the polymer. The butyl isocyanate is slowly added to the copolymer in a suitable enclosed reactor equipped with a stirrer and other conventional equipment at room temperature over a 30-minute time period. The reaction mass undergoes a mild exotherm shortly after the addition. After 8 hours, infrared analysis is used to analyze the reaction mass. The reaction is continued until the butyl isocyanate is reduced to a desired level. The modified polymer containing N-butyl carbamoyloxyalkanoyoxyalkyl groups is stripped of any residual isocyanate and then stored for future use as an intermediate in preparing coating compositions.

Example 20. Fifty grams (0.233 moles or equivalents) of the Preparation A methacrylate ester are placed in a reactor equipped with a stirrer, feeding port, and means of temperature measurement and control. The methacrylate ester is heated to 80°C and 0.23 equivalents of phthalic anhydride are slowly added. The temperature is then increased to 120°C and held there for 2 hours after which time the reaction mass is cooled to room temperature and stored for future use.

Although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby; but rather, the invention encompasses the generic area as hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

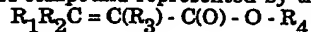


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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A compound represented by the formula:



wherein:

$R_1$ ,  $R_2$  and  $R_3$  are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue;

$R_4$  is a substituted or unsubstituted monovalent hydrocarbon residue represented by the formula:  
 $-(CR_5R_6)_v - (CR_7R_8)_w - (C(OH)R_9)_x - (CR_{10}R_{11})_y - (CR_{12}R_{13})_z - R_{14}$

wherein:

each  $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$  and  $R_{13}$  are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue;

$R_{14}$  is hydrogen, hydroxyl or a substituted or unsubstituted monovalent hydrocarbon residue provided  $R_{14}$  is hydroxyl when  $x$  is value of 0 and  $R_{14}$  is other than hydroxyl when  $x$  is a value of 1;

each of  $v$ ,  $w$ ,  $y$  and  $z$  is a value of from 0 to about 5 and the sum of  $v + w + x + y + z$  is a value of from about 3 to about 15; and  $x$  is a value of 0 or 1;

provided (i) at least one of  $w$  and  $y$  is a value other than 0 when  $x$  is a value of 1; (ii) at least one of  $R_7$ ,  $R_8$ ,  $R_9$ ,  $R_{10}$  and  $R_{11}$  is other than hydrogen when  $x$  is a value of 1; and (iii) at least one of  $R_{12}$  and  $R_{13}$  is other than hydrogen when  $x$  is a value of 0.

2. The compound of claim 1 which is selected from 2-ethyl-3-hydroxyhexyl methacrylate, 1-propyl-2-ethyl-3-hydroxypropyl methacrylate, 1-ethyl-2-methyl-3-hydroxypropyl methacrylate, 2-methyl-3-hydroxypentyl methacrylate, 2-propyl-3-hydroxyheptyl methacrylate, 1-butyl-2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxyheptyl methacrylate, 1-butyl-2-ethyl-

3-hydroxypropyl methacrylate, 2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxypropyl methacrylate, 1-i-butyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-methyl-3-hydroxypropyl acrylate, 1-i-butyl-3-hydroxypropyl methacrylate, 3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-butyl-3-hydroxypropyl methacrylate, 2-butyl-3-hydroxybutyl methacrylate, 1-i-propyl-2,2-dimethyl-3-hydroxypropyl methacrylate, and 2,2-dimethyl-3-hydroxy-4-methylpentyl methacrylate.

3. A process for producing the compound of claim 1 which is selected from:

- (i) an esterification process comprising reacting a diol compound with methacrylic acid or acrylic acid to produce the compound;
- (ii) a process comprising reacting a diol compound with methacrylic anhydride or acrylic anhydride to produce the compound; or
- (iii) a transesterification process comprising reacting a diol compound with alkyl methacrylate or alkyl acrylate to produce the compound.

4. The process of claim 3 further comprising derivatizing the compound in which the derivatizing reaction comprises an oxidation, alkoxylation, carboxylation, reduction, carbamoylation, hydrogenation, dehydrogenation, condensation, amination, esterification, etherification, silylation, alkylation or acylation reaction.

5. The product produced by the process of claims 3 or 4.

6. A reactive surfactant comprising an alkoxyated derivative of a compound of claim 1 or a wet adhesion monomer comprising a product produced by the process of claim 3.

7. A copolymer comprising the reaction product of (a) one or more hindered-hydroxyl functional (meth)acrylate monomers and (b) at least one other monomer copolymerizable therewith, said copolymer having (i) a number average molecular weight of less than about 12,000, (ii) a glass transition temperature of from -30°C to about 100°C, and (iii) a styrene concentration of from 0 to less than about 20 weight percent, and said hindered-hydroxyl functional (meth)acrylate monomer having a diacrylate content of less than about 5 weight percent.

8. The copolymer of claim 7 in which the hindered-hydroxyl functional (meth)acrylate monomer is a compound of claim 1.

9. The copolymer of claim 7 in which the hindered-hydroxyl functional (meth)acrylate monomer is selected from one or more of 2-ethyl-3-hydroxyhexyl methacrylate, 1-propyl-2-ethyl-3-hydroxypropyl methacrylate, 1-ethyl-2-methyl-3-hydroxypropyl methacrylate, 2-methyl-3-hydroxypentyl methacrylate, 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 2-propyl-3-hydroxyheptyl methacrylate, 1-butyl-2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxyheptyl methacrylate, 1-butyl-2-ethyl-3-hydroxypropyl methacrylate, 2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxypropyl methacrylate, 1-i-butyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-methyl-3-hydroxypropyl acrylate, 1-i-butyl-3-hydroxypropyl methacrylate, 3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-butyl-3-hydroxypropyl methacrylate, 2-butyl-3-hydroxybutyl methacrylate, 1-

i-propyl-2,2-dimethyl-3-hydroxypropyl methacrylate, and 2,2-dimethyl-3-hydroxy-4-methylpentyl methacrylate.

10. The copolymer of claim 7 in which the other copolymerizable monomer is selected from one or more other (meth)acrylates, hydroxyalkyl (meth)acrylates and vinyl compounds.

11. A composition comprising (a) a hindered-hydroxyl functional (meth)acrylate-containing copolymer of claim 7 and (b) a crosslinking agent.

12. The composition of claim 11 in which the hindered-hydroxyl functional (meth)acrylate monomer is selected from one or more of 2-ethyl-3-hydroxyhexyl methacrylate, 1-propyl-2-ethyl-3-hydroxypropyl methacrylate, 1-ethyl-2-methyl-3-hydroxypropyl methacrylate, 2-methyl-3-hydroxypentyl methacrylate, 2,2,4-trimethyl-3-hydroxypentyl methacrylate, 2-propyl-3-hydroxyheptyl methacrylate, 1-butyl-2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxyheptyl methacrylate, 1-butyl-2-ethyl-3-hydroxypropyl methacrylate, 2-propyl-3-hydroxypropyl methacrylate, 2-ethyl-3-hydroxypropyl methacrylate, 1-i-butyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-i-propyl-3-hydroxypropyl methacrylate, 2-i-propyl-3-methyl-3-hydroxypropyl acrylate, 1-i-butyl-3-hydroxypropyl methacrylate, 3-hydroxy-5-methylhexyl methacrylate, 1-methyl-2-butyl-3-hydroxypropyl methacrylate, 2-butyl-3-hydroxybutyl methacrylate, 1-i-propyl-2,2-dimethyl-3-hydroxypropyl methacrylate, and 2,2-dimethyl-3-hydroxy-4-methylpentyl methacrylate.

13. The composition of claim 11 in which the other copolymerizable monomer is selected from one or more other (meth)acrylates, hydroxyalkyl (meth)acrylates and vinyl compounds.

14. The composition of claim 11 in which the crosslinking agent is selected from aminoplasts, multifunctional isocyanates, phenolics, cycloaliphatic epoxides, glycidyl epoxides, carbodiimides and polycarbodiimides.

15. A method of protecting a surface from corrosion when exposed to an acidic or alkaline environment which comprises applying to the surface a composition comprising (a) a hindered-hydroxyl functional (meth)acrylate-containing copolymer and (b) a crosslinking agent, and curing said composition.

16. A curable coating composition comprising the copolymer of claim 7 and a crosslinking agent, and a cured film prepared therefrom.

17. The curable coating composition of claim 16 which is cured with actinic or thermal energy or a mixture thereof.

18. An adhesive ink or sealant composition comprising the copolymer of claim 7 and a crosslinking agent, or a water-borne, solvent-borne, powdered, colored or clear coating comprising the copolymer of claim 7.

**SUBSTITUTE**  
***REMPLACEMENT***

**SECTION is not Present**  
***Cette Section est Absente***